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HOMOGENEOUS NUCLEATION IN CONTAMINATED ATMOSPHERES

Edward Y. H. Keng, et al

Georgia Institute of Technology

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FINAL TECHNICAL REPORT

PROJECT B-364

HOMOGENEOUS NUCLEATION IN CONTAMINATED ATMOSPHERES

EDWARD Y. H. KENG, FU-CHU WEN, AND CLYDE ORR, JR.

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GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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WASHINGTON, D.C. 20201

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I. SUMMARY

Homogeneous nucleation of sodium chloride and potassium iodide solution droplets suspended in air was studied. The supersaturation was created by lowering the humidity of the air, and the times required to achieve nucleation at various humidities were measured. Equations were derived to evaluate the kinetic constant and the interfacial energy from the induction time data and the estimated values of solute activity. The results appear to be reasonable. Pollutants such as lead ions and sulfur dioxide were found not to affect the nucleation mechanism to a detectable level.

Nucleation of droplets on threads and flat surfaces was also investigated. This heterogeneous nucleation was observed with a microscope. The nucleation in these cases occurred at much lower supersaturations than that of homogeneous nucleation. The droplets converted to crystals almost at the same time regardless of size. Their conversion does not follow the probability relation. The time required for nucleation to take place was very sensitive to the type of surface that supported the droplets. The presence of lead ions was found greatly to increase the induction time of heterogeneous nucleation.

II. INTRODUCTION

The behavior of hygroscopic particles in the atmosphere under various humidity conditions has long been of interest to the field of atmospheric science. These particles absorb water vapor from the atmosphere and dissolve into droplets at high humidities. The condensation process is simple and well understood. However, when the humidity is decreased to a level lower than the humidity at which the droplets are formed, the droplets do not readily give up all the water until a much lower humidity condition is reached. Often a long waiting time is required. The mechanism of this process is closely related to the nucleation process and it has caused much confusion in the past. This study was undertaken to reveal some of the behavior of solution droplets in this region.

Sodium chloride was chosen to be the primary substance of investigation because of its prevalence in the atmosphere and its significance in atmospheric phenomena. Potassium iodide was also employed due to its low interfacial energy compared to that of sodium chloride. Substances having lower interfacial energy are less sensitive to a supersaturation change, thus offering a wider range of supersaturations for nucleation examination.

Experimental studies of homogeneous nucleation in solutions are very rarely performed. Methods that exclude the effects of container wall or other catalytic agent are difficult. However, if this is not accomplished heterogeneous nucleation takes place before homogeneous nucleation can start. The nucleation of airborne droplets is believed to be homogeneous. If this is true, the methods suggested in this study can be used to evaluate the kinetic constant and interfacial energy in solution systems and assist in the development or verification of nucleation theory.

Condensation on hygroscopic particles attached to a surface is similar to that on airborne particles. But nucleation phenomena are quite different. Droplets on surfaces undergo heterogeneous nucleation at much higher humidity conditions than is the case with airborne droplets. The effects of surfaces on nucleation have been realized for a long time, but very little is known of their nature. This study was designed to reveal some of the characteristics of nucleation of solution droplets on various surfaces.

III. HOMOGENEOUS NUCLEATION THEORY

A. Introduction

Nucleation is a phase transformation process; it can either be from a vapor phase to a liquid or solid phase or from a liquid phase to a solid phase. When a new phase is formed in a homogeneous mother phase in the absence of foreign surfaces and catalytic agents, the process is called homogeneous nucleation. Otherwise, the process is called heterogeneous nucleation. Nucleation theory as has been developed relates mainly to homogeneous nucleation. Due to the complexities of the effects of a foreign surface or a catalytic agent, only special heterogeneous nucleation cases have been discussed.

The classical theory of homogeneous nucleation was developed in 1926 by Volmer and Weber.[1] It is based on the principles of thermodynamics and kinetics of a supersaturated phase. Later development includes employing statistical mechanics and considerations using the microscopic properties of clusters.[2] Due to the lack of reliable and sufficient experimental data, progress toward verification of nucleation theory has been very slow. Details of the nucleation theory and its development have been reported by many investigators[3-31]; they will not be repeated here.

B. Induction Time

Nucleation may not occur immediately after the supersaturation of the system is attained. This is especially true when solutions are involved. The time interval between the creation of the supersaturated state and the occurrence of nucleation is called the induction time. Sometimes it is also called induction period, time lag, or waiting time. The length of the induction time is a function of the following parameters: the degree of supersaturation, the composition and

state of the mother phase, the presence of impurity particles, the physical properties of the clusters, foreign surfaces, and other physical disturbances. In this study, emphasis is placed on the degree of supersaturation and the physical properties of the clusters.

The induction time has caused some confusion in the past due to the complications of nucleation phenomena. Four periods are actually involved in nucleation experiments. The first is the time required to achieve the supersaturated state. This time, say t_1, is dependent on the method used. For example, if the mother phase is cooled to achieve the supersaturated state, t_1 depends on the cooling rate. Once the supersaturated state is developed, the cluster distribution must readjust itself to the new condition. The period required for readjusting, say t_2, is dependent on the degree of supersaturation and the properties of the clusters. When the new condition is developed slowly, the cluster distribution starts to adjust before the final state is fully developed. If t_2, in this case, starts when the final state is obtained, it would also be dependent on t_1 in addition to other factors. Theoretically t_2 is often defined as the time required to attain the steady state of cluster distribution from single molecules or a given cluster distribution when the supersaturated state is suddenly created. The third period, t_3 starts from the time the steady state of cluster distribution is achieved to the time that critical nuclei are formed. Nucleation is a kinetic phenomenon and a rate process; not all the critical nuclei are formed at one time. This stage may be considered to end when the rate of nucleation reaches a constant value. The fourth period, t_4, is the time required for a critical nucleus to grow to detectable dimensions. This period may be estimated from the growth rate value.

The first period and fourth period present no problems. The first period

is considered only in experimental studies. The fourth period is considered growth process. Only the second and the third periods are included within the main scope of nucleation theory.

C. Derivation of Equations

When small, aqueous droplets containing hygroscopic substances are exposed to low humidity conditions, a supersaturated state is quickly achieved. The time required can be estimated from the evaporation rate; it is very brief and is assumed to be negligible for a submicron droplet. The experimentally measured induction time can be reasonably assumed to be the period from the initiation of the supersaturated state to the critical cluster formation, since the time for growth processes of a small crystal at a high supersaturation is also very small.

According to homogeneous nucleation theory, clusters of different size are the results of the stepwise addition of molecules.[3] Assuming that the cluster c_x, containing x molecules, can have transition only to their next nearest neighbors c_{x+1} or c_{x-1} and the degree of supersaturation is constant, the probability of finding a cluster c_x at time t, $p(x,t)$, may be expressed in a form similar to the Fokker-Planck equation[31]

$$\frac{\partial p(x,t)}{\partial t} = \frac{\partial}{\partial x} \left\{ D(x)\ P^{o}(x)\ \frac{\partial}{\partial x} \left[\frac{p(x,t)}{p^{o}(x)} \right] \right\} \qquad (1)$$

where $D(x)$ is the net probability per unit time of a monomer joining a cluster c_x and $p^{o}(x)$ the probability of finding a cluster c_x at equilibrium. Many investigators[32-45] have solved this equation with different assumptions. However, the basic assumptions may be summarized as

Initial condition: $p(x,o) = 0$ at $t = 0$

Boundary conditions: $p(1,t) = p^{o}(1)$ for all t

$p(x,t) = 0$ for $x > x^*$

where x^* is the number of molecules in a critical cluster. The solution may be written in the general form

$$p(x,t) = Z[1 - e^{-t/\tau_1}] \exp\left[-\frac{\Delta G(x)}{kT}\right] \tag{2}$$

where Z is the Zeldovich factor, τ_1 the relaxation time to approach the steady-state cluster distribution, $\Delta G(x)$ the free energy change accompanying the formation of the cluster c_x, k the Boltzmann constant, and T the absolute temperature. The relaxation time to approach a steady state of cluster distribution is expressed by[40,41,42]

$$\tau_1 = -\frac{kT}{D(x^*)\left\{\frac{d^2[\Delta G(x)]}{dx^2}\right\}_{x=x^*}} \tag{3}$$

If t_i is assumed to be the time for the distribution of clusters to reach 99% of the steady state value, then t_i may be approximated by[42]

$$t_i = 5\tau_1 = -\frac{5kT}{D(x^*)\left\{\frac{d^2[\Delta G(x)]}{dx^2}\right\}_{x=x^*}} \tag{4}$$

The relaxation time τ_1 is estimated to be of the order of microseconds for high-supersaturation system and is assumed to be negligible in this study. The Zeldovich factor does not apply after the steady-state distribution of cluster formation is approached, i.e., no flux of probability, in a small

droplet system. Thus the probability of the occurrence of a critical cluster can be approximated by a simple relation

$$p^* = \frac{N^*}{N_1} = \exp\left[- \frac{\Delta G^*}{kT} \right] \tag{5}$$

where N^* and N_1 are the numbers of the critical clusters and the single molecules per unit volume of the mother phase, respectively, and ΔG^* the free energy change accompanying the formation of the critical nucleus.

If the probability of occurrence in a single trial is p, the probability of an event not occurring in n trials is [46,47]

$$1 - W = (1 - p)^n \tag{6}$$

where W is the probability that the event will occur in n trials. If a supersaturated droplet is under consideration, the probability that the nucleation will occur in time t is

$$W = 1 - [1 - VN_1 p^*]^{n^* t} \tag{7}$$

where V is the volume of the droplet and n^* the total number for arrival of the post-critical entity at a critical cluster surface per unit time. The probability term p^* may be defined as the chance of having a critical cluster for each of the monomers existing in the system. The product of VN_1 is the total number of monomers in a droplet and $n^* t$ is the number of trials in time t. Since $V N_1 p^*$ is very small, equation 7 may be simplified to

$$W = 1 - \exp[-AVp^* t] \tag{8}$$

where A is the product $n^* N_1$ and is called the kinetic constant or the pre-exponential factor in nucleation rate equations. This is shown by the nucleation rate equation

$$J = n^* N^* = n^* N_1 \exp\left[- \frac{\Delta G^*}{kT} \right] \tag{9}$$

where J is the nucleation rate per unit volume of the mother phase.

Equation 8 may be rewritten as

$$W = 1 - \exp\left[- \frac{t}{\tau_2} \right] \tag{10}$$

where

$$\frac{1}{\tau_2} = AVP^* = AV \exp\left[- \frac{\Delta G^*}{kT} \right] \tag{11}$$

Letting θ be the time in which a droplet is 99% certain to nucleate or that 99% of all the droplets will nucleate, then

$$\theta = 5\tau_2 = \frac{5}{AV \exp\left[- \frac{\Delta G^*}{kT} \right]} \tag{12}$$

or

$$\ell n\ \theta = - \ell n \left(\frac{AV}{5} \right) + \frac{\Delta G^*}{kT} . \tag{13}$$

IV. PROPERTIES OF SUPERSATURATED SOLUTIONS

A. Supersaturation and Vapor Pressure

The techniques used in this study are most suitable for hygroscopic materials. The temperature and pressure of the system were kept constant; humidity was thus the only operating parameter controlling the concentration of the solution droplets. Nucleation has been ordinarily discussed in terms of supersaturation or other terms related to the solution concentration, thus the dependence of solution concentration on humidity is vitally important in this study.

Experimental data on the vapor pressure of aqueous solutions are generally not available in the supersaturated region. Values have most often been obtained by extrapolation from the unsaturated region and guided by other similar materials. Various methods have been proposed in the past, but the approach suggested by Hidalgo[48,49] seems to be very satisfactory for chloride compounds.

The osmotic coefficient data of the aqueous solutions of cesium chloride and lithium chloride[50] are used as a guide for the extrapolation of other alkali chloride. The extrapolations for sodium and potassium chlorides are shown in Figure 1.

The activity of water in an aqueous solution, a_w, can be calculated from the extrapolated osmotic coefficients by the following equation[51]

$$a_w = \exp\left[- \frac{\phi \nu m M_w}{1000} \right] \qquad (14)$$

where ϕ is the osmotic coefficient of the solution, ν the number of ions

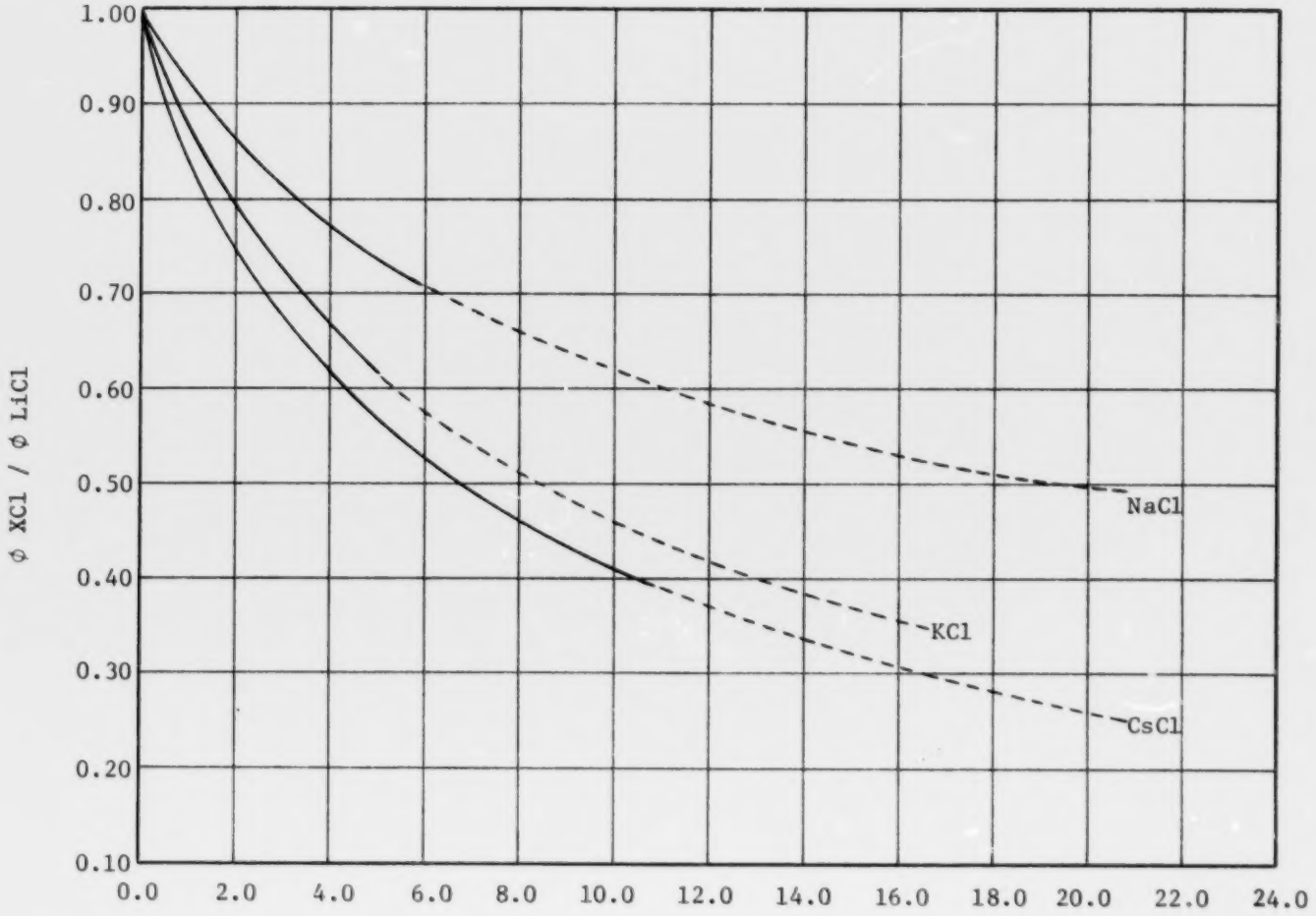

Figure 1. Osmotic Coefficient Ratios of the Alkali Chlorides Relative to Lithium Chloride in Aqueous Solutions at 25°C.

per molecule of solute, m the solution molality, and M_w the molecular weight of solvent, i.e., water in this case.

The partial vapor pressure of water in equilibrium with an aqueous solution at temperature T may be evaluated by the following equation:

$$\ell n\ P = \ell n\ a_w + \ell n\ P_o + \int_{P_o}^{P} \frac{\alpha}{RT}\, dP \qquad (15)$$

where P_o is the vapor pressure of water and α the coefficient of compressibility of the solution. The integral term in equation 15 is usually smaller than the experimental error in vapor pressure measurements. Therefore, equation 15 may be simplified to

$$P = a_w P_o \qquad (16)$$

Thus the concentration of the solution droplets in equilibrium at various humidity conditions may be calculated from equations 14 and 16. The concentration, expressed in molality, of the aqueous solutions at equilibrium state is plotted against the relative humidity and is presented in Figure 2. Curvature effects are very small and are not considered here.

Difficulties were encountered when the above method was employed to extrapolate potassium iodide data. The molality of potassium iodide solutions at which nucleation has been observed is beyond the value of 30. The above method is reliable for predicting the properties of supersaturated solutions of chloride salts only up to 20 molality. Even though the potassium iodide curve may be extrapolated as in Figure 1 to higher concentrations, experimental osmotic coefficients for lithium chloride solutions are not

available. Furthermore, extrapolation of the osmotic coefficient beyond the experimental value is not recommended due to the shape of the curve (see figure in reference 48). An alternative method is proposed here. The behavior of the humidity curve of potassium iodide is assumed to be similar to that of potassium chloride shown in Figure 2. These curves are extrapolated to 40 molality. The osmotic coefficients of potassium iodide solutions are then calculated from the extrapolated values of the curve KI in Figure 2 using equations 14 and 16. The result is presented in Figure 3. The sodium chloride curve of Figure 3 was obtained by extrapolation of the osmotic coefficient ratios.[48,49]

The extrapolated values for sodium chloride solutions up to 13.85 molality were used in this study. The procedure was verified by Hidalgo[48,49] to be very reliable. The uncertainty involved in the extrapolation outlined above for aqueous potassium iodide solutions is not known. In order to understand more fully the significance of the possible error associated with the long range extrapolation on the final data analysis, two other arbitrary extrapolation curves were drawn in Figure 2. One curve, KI(H), shows considerably higher concentrations than the original curve, KI, when the solutions were in equilibrium at the same humidity conditions. The other curve, KI(L), gives lower concentration values. The possible consequences of high or low extrapolation are discussed in Section VI.

B. Activity Coefficients and Activities

Nucleation time and nucleation rate are both functions of a_1/a_o, where a_1 is the activity of the solute at the supersaturation and a_o the activity of the solute at saturated condition. A numerical integration was used to evaluate the activity coefficient employing the Gibbs-Duhem relation in the

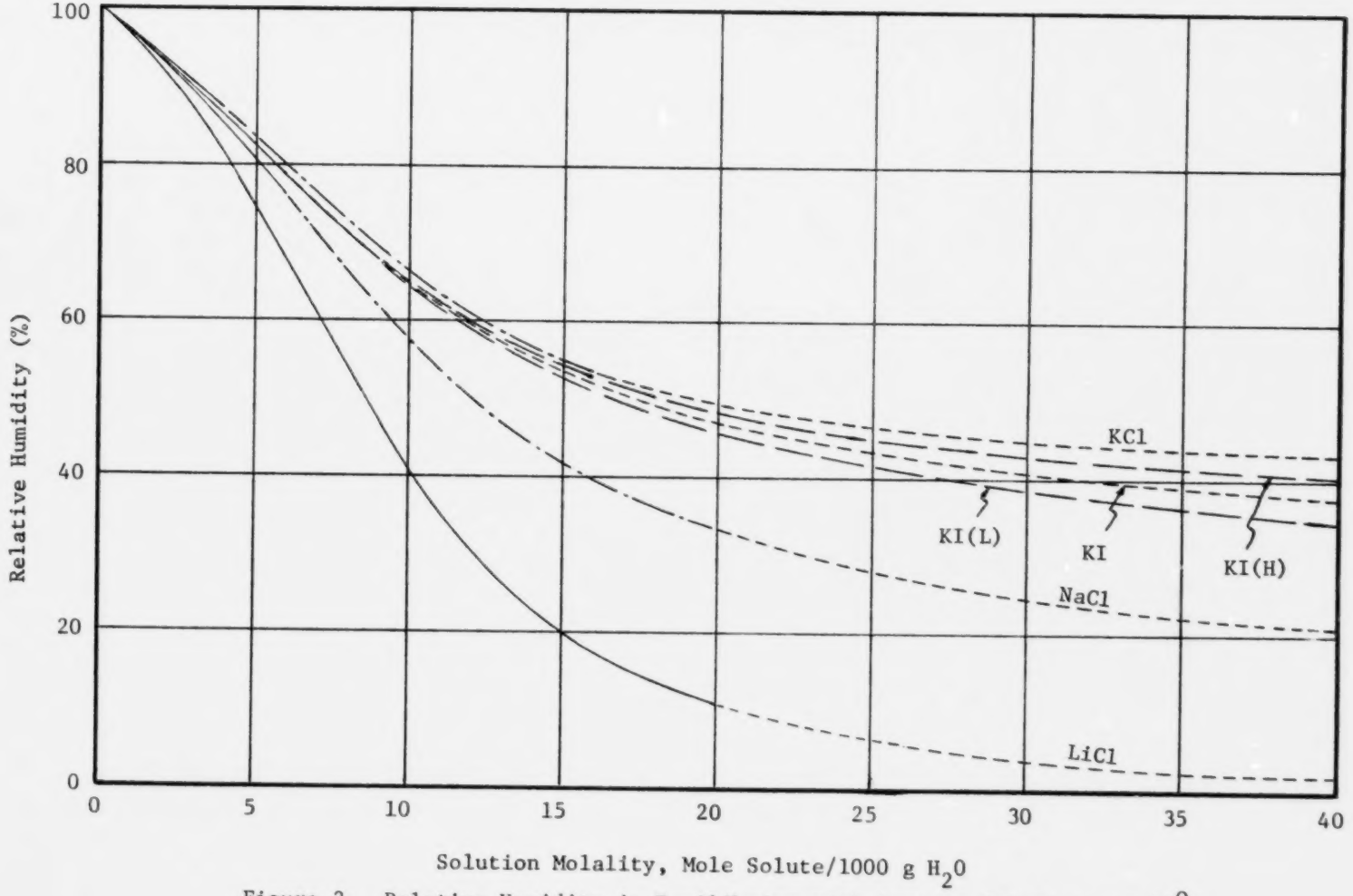

Figure 2. Relative Humidity in Equilibrium with Aqueous Solutions at 25°C.

_____ Experimental Data ---- Extrapolation by These Authors

—·— Extrapolation by Hidalgo[48] __ __ Arbitrary Extrapolation for Error Analysis

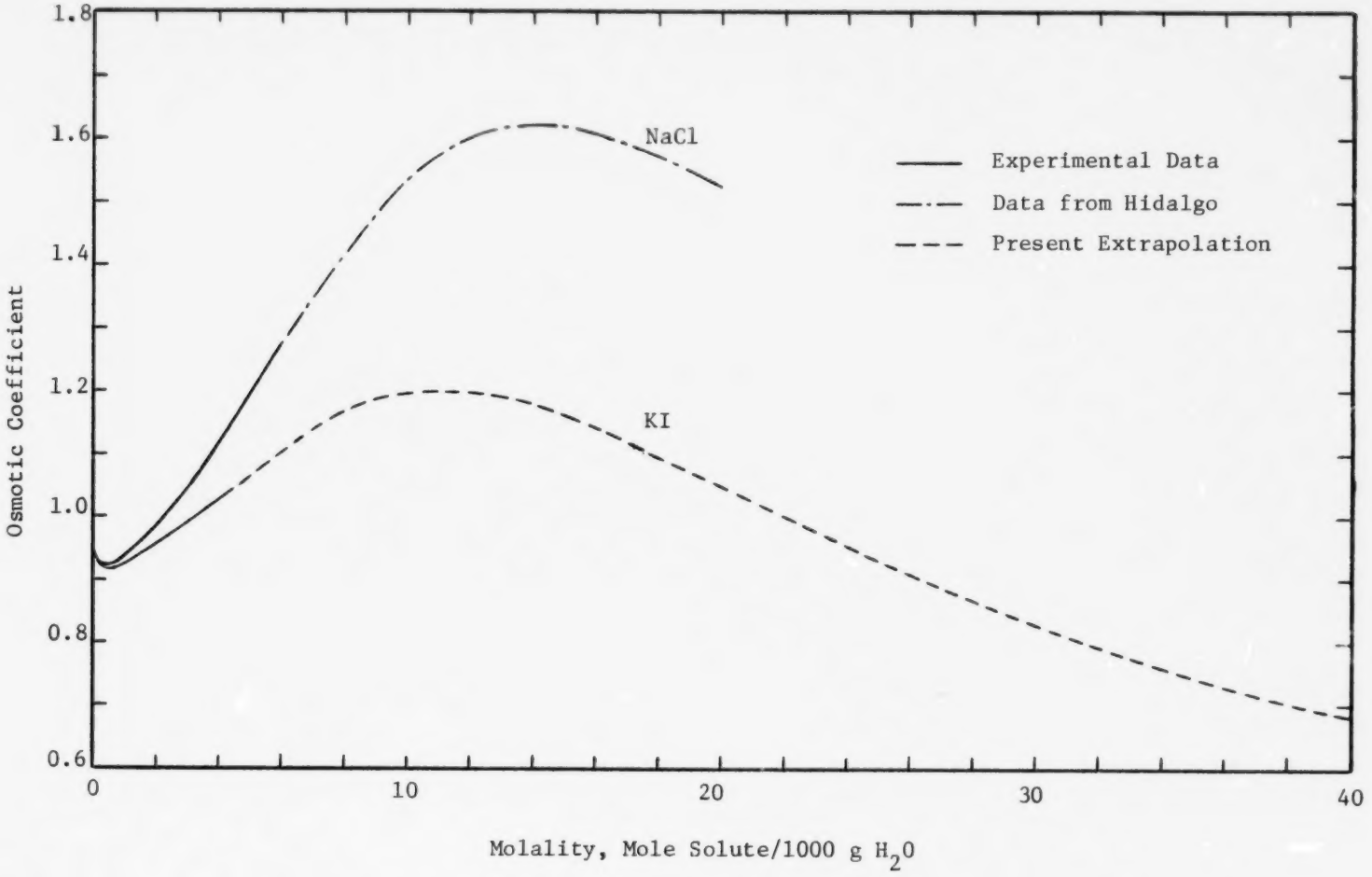

Figure 3. Osmotic Coefficient of Aqueous Solutions at 25°C.

form[49]

$$d(\ell n\ \gamma_{\pm}) = -\frac{1}{m}\, d[m(1 - \phi)] \qquad (17)$$

where $\gamma_{\pm}$ is the mean molal activity coefficient of the solute. The equation may be rearranged and integrated yielding

$$\gamma_{\pm} = (\gamma_{\pm})_o \exp\left[(\phi - \phi_o) - \int_{m_o}^{m} \left(\frac{1-\phi}{m}\right) dm\right] \qquad (18)$$

the detailed evaluation procedure being given by Hidalgo.[48] The value chosen for m_o was 0.1 and corresponding values for $(\gamma_{\pm})_o$ and ϕ_o were taken from experimental data.

The activity of the solute, a_1, was then calculated from

$$a_1 = (\gamma_{\pm} m)^{\nu} \qquad (19)$$

Values of a_1 and other properties of sodium chloride solutions evaluated by Hidalgo[48] are summarized in Table I. The properties of potassium iodide are presented in Table II. Activities were calculated from the osmotic coefficients estimated from the extrapolated curve (KI) of Figure 2. The values of $\ell n^{-2}(a_1/a_o)$ at 25°C plotted against the concentration of the solutions are presented in Figures 4 and 5.

TABLE I. PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS AT 25°C[48]

Molality	Osmotic Coefficient	Water Activity	Solute Activity	$\ln -2\left(\frac{a_1}{a_o}\right)$
.20	.9245	.99335	.2159,-1	
.40	.9203	.98682	.7689,-1	
.60	.9230	.98024	.1631,0	
.80	.9288	.97358	.2812,0	
1.00	.9355	.96685	.4319,0	
1.20	.9428	.96005	.6172,0	
1.40	.9513	.95314	.8406,0	
1.60	.9616	.94607	.1107,1	
1.80	.9723	.93888	.1421,1	
2.00	.9833	.93159	.1785,1	
2.20	.9948	.92417	.2205,1	
2.40	1.0068	.91661	.2689,1	
3.00	1.0453	.89315	.4589,1	
3.50	1.0796	.87271	.6818,1	
4.00	1.1158	.85144	.9826,1	
4.50	1.1531	.82947	.1382,2	
5.00	1.1916	.80680	.1912,2	
5.50	1.2309	.78353	.2605,2	
6.00	1.2706	.75980	.3506,2	
6.50	1.3065	.73639	.4630,2	32.490
7.00	1.3440	.71249	.6074,2	5.007
7.50	1.3827	.68821	.7921,2	1.970
8.00	1.4170	.66467	.1016,3	1.082
8.50	1.4505	.64130	.1293,3	0.692
9.00	1.4810	.61861	.1625,3	0.488
9.50	1.5070	.59699	.2011,3	0.370
10.00	1.5300	.57620	.2461,3	0.293
10.50	1.5538	.55551	.3000,3	0.239
11.00	1.5720	.53629	.3599,3	0.202
11.50	1.5855	.51841	.4255,3	0.175
12.00	1.6000	.50066	.5016,3	0.153
12.50	1.6084	.48460	.5814,3	0.137
13.00	1.6160	.46909	.6700,3	0.123
13.50	1.6211	.45450	.7648,3	0.113
14.00	1.6222	.44117	.8624,3	0.104
14.50	1.6210	.42873	.9641,3	0.0970
15.00	1.6180	.41707	.1069,4	0.0910
15.50	1.6121	.40642	.1175,4	0.0860
16.00	1.6080	.39572	.1291,4	0.0815
16.50	1.5981	.38669	.1396,4	0.0780
17.00	1.5900	.37759	.1511,4	0.0746

continued

TABLE I (CONCLUDED)

Molality	Osmotic Coefficient	Water Activity	Solute Activity	$\ell n^{-2\left(\frac{a_1}{a_o}\right)}$
17.50	1.5800	.36924	.1624,4	0.0718
18.00	1.5680	.36169	.1733,4	0.0693
18.50	1.5577	.35403	.1849,4	0.0670
19.00	1.5490	.34629	.1974,4	0.0648
19.50	1.5372	.33957	.2089,4	0.0630
20.00	1.5260	.33297	.2207,4	0.0613

TABLE II. PROPERTIES OF AQUEOUS POTASSIUM IODIDE SOLUTIONS AT 25°C

Molality	Osmotic Coefficient	Water Activity	Solute Activity	$\ell n^{-2}\left(\frac{a_1}{a_o}\right)$
0.20	0.922	0.993	.2149,-1	
0.40	0.917	0.987	.7596,-1	
0.60	0.918	0.980	.1602,0	
0.80	0.922	0.974	.2737,0	
1.00	0.926	0.967	.4160,0	
1.20	0.931	0.961	.5898,0	
1.40	0.937	0.954	.7953,0	
1.60	0.943	0.947	.1036,1	
1.80	0.950	0.940	.1311,1	
2.00	0.957	0.933	.1623,1	
2.50	0.974	0.916	.2592,1	
3.00	0.990	0.899	.3826,1	
3.50	1.006	0.881	.5368,1	
4.00	1.021	0.863	.7247,1	
4.50	1.032	0.846	.9446,1	
5.00	1.061	0.826	.1249,2	
6.00	1.102	0.788	.2012,2	
7.00	1.141	0.750	.3074,2	
8.00	1.169	0.714	.4421,2	
9.00	1.189	0.680	.6073.2	1761.2
10.00	1.196	0.650	.7930,2	11.839
11.00	1.198	0.622	.1001,3	3.652
12.00	1.197	0.596	.1229,3	1.881
13.00	1.193	0.572	.1475,3	1.204
14.00	1.178	0.552	.1707,3	0.894
15.00	1.161	0.534	.1941,3	0.711
16.00	1.141	0.518	.2160,3	0.599
17.00	1.119	0.504	.2371,3	0.521
18.00	1.094	0.492	.2559,3	0.468
19.00	1.072	0.480	.2756,3	0.424
20.00	1.048	0.470	.2928,3	0.392
21.00	1.023	0.461	.3077,3	0.369
22.00	0.999	0.453	.3225,3	0.349
23.00	0.977	0.445	.3373,3	0.331
24.00	0.952	0.439	.3479,3	0.319
25.00	0.929	0.433	.3591,3	0.308
26.00	0.908	0.427	.3695,3	0.299
27.00	0.887	0.422	.3798,3	0.290
28.00	0.867	0.417	.3886,3	0.283
29.00	0.849	0.412	.3981,3	0.276
30.00	0.829	0.408	.4052,3	0.271

continued

TABLE II. (CONCLUDED)

Molality	Osmotic Coefficient	Water Activity	Solute Activity	$\ell n^{-2\left(\frac{a_1}{a_o}\right)}$
31.00	0.811	0.404	.4124,3	0.266
32.00	0.795	0.400	.4205,3	0.261
33.00	0.779	0.396	.4270,3	0.257
34.00	0.762	0.393	.4321,3	0.253
35.00	0.747	0.390	.4382,3	0.250
36.00	0.732	0.387	.4437,3	0.247
37.00	0.718	0.384	.4484,3	0.244
38.00	0.705	0.381	.4537,3	0.242
39.00	0.692	0.378	.4591,3	0.239
40.00	0.681	0.375	.4648,3	0.236

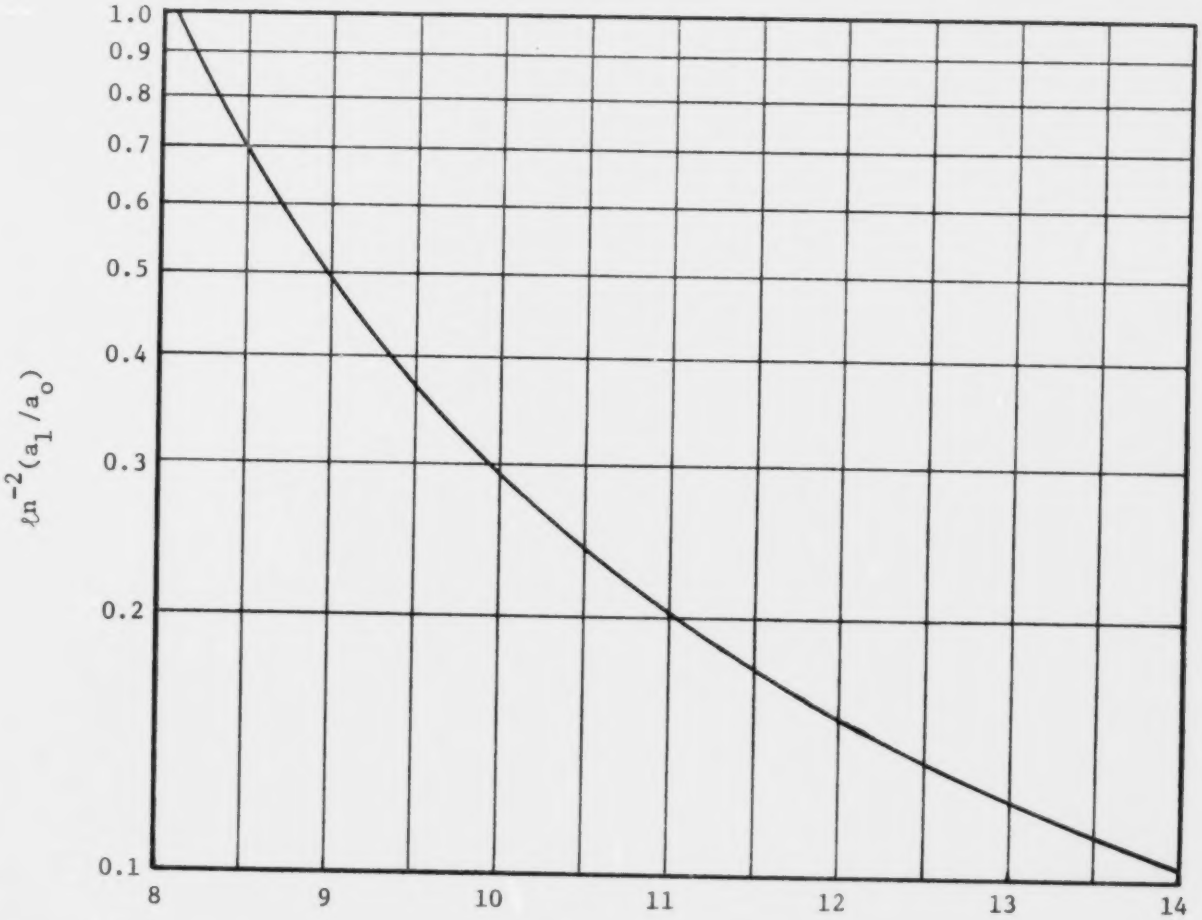

Figure 4. $Ln^{-2}(a_1/a_o)$ of Aqueous Sodium Chloride Solutions at 25°C.

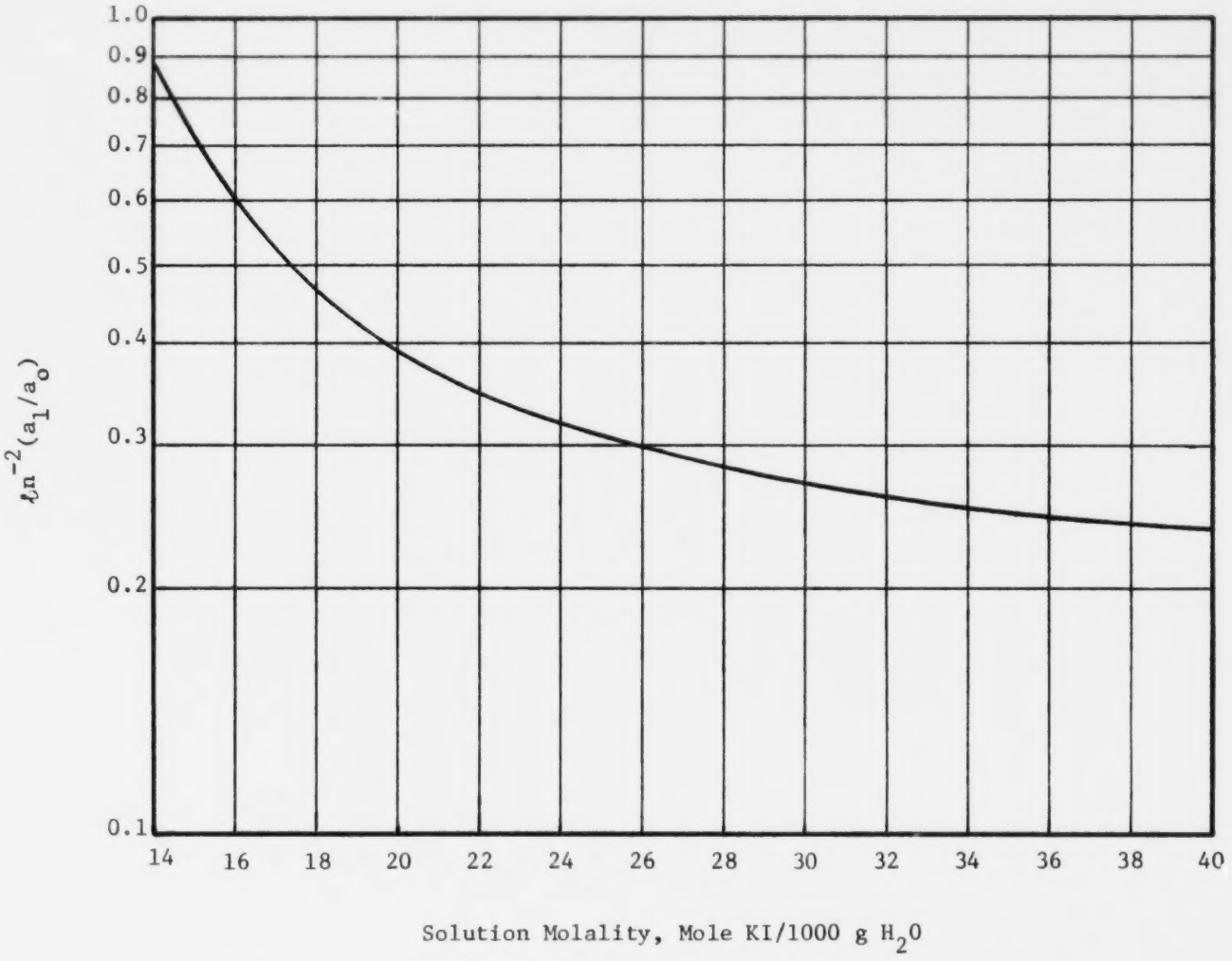

Figure 5. $Ln^{-2}(a_1/a_o)$ of Aqueous Potassium Sodide Solutions at 25°C.

V. AIRBORNE DROPLET TECHNIQUES

A. Ion Mobility System

A radial-flow ion mobility analyzer was used to detect the occurrence of nucleation of sodium chloride droplets of 0.02 micron in diameter. Similar systems have been employed in several previous studies.[52,53,54] Since there was the possibility that the experimental system used by Hidalgo[48] might have been biased by heaters within the analyzer, the analyzer employed in this study had no heaters. A detailed description of the present system is presented in the following section:

1. General operation and apparatus

Aerosols of sodium chloride droplets were generated by atomizing salt solutions with a modified Devilbiss No. 180 atomizer. A quart-size glass container was used to retain the solution, and the container was immersed in ice water to minimize evaporation. Large droplets were eliminated by a large impaction plate in the atomizer and a collector connected to the exit of the atomizer. Aerosols thus produced were found satisfactory with a solution concentration of 0.05% without further treatments other than moisture control. Incoming air was filtered and divided into two equal portions. One went to the atomizer and the other to a humidity controlled chamber. The final humidity was established by mixing these two streams. This arrangement assured consistent aerosol concentration and particle size distribution on a dry crystal basis for all operating conditions.

The aerosol was cooled to a temperature about $2^{o}F$ above the dew point in a conditioning chamber. Therefore, all aerosols coming out of the conditioning chamber contained only solution droplets. The aerosol then entered a residence

chamber after passing through a coil of copper tubing where it attained room temperature. A fan was used to circulate room air around the copper tubing. The time required for the aerosol to pass through the copper tubing was only about two seconds. A thermometer was placed at the exit of the copper tubing; temperatures measured were always within $0.2^{\circ}F$ of the room temperature. The elapsed time after leaving the copper coil when the aerosol was led directly to the ion mobility analyzer was about 5 seconds. The residence chamber offered delays from 30 to 240 seconds by selecting the exit point and aerosol flow rate. The dew point temperature was measured by a Cambridge Systems Thermoelectric Dew Point Hygrometer, Model 990-B. This unit was repeatedly calibrated with air of known dew point temperatures. The accuracy of relative humidity measurements is thus believed to be within $\pm$ 0.5 per cent. The relative values among measured relative humidities were better than $\pm$ 0.2 per cent.

The ion mobility analyzer consisted essentially of two, flat, circular, parallel plates. The separation between the two plates was fixed at 0.0787 inch. The plates were mounted inside a metal enclosure and insulated from it with Teflon insulators. Heaters were not used in the ion mobility analyzer in this investigation. Instead, the inner surface of the whole upper half of the metal enclosure was covered with a machined Teflon lining. This Teflon lining prevented the two Teflon insulators from collecting successive particle deposits while permitting the aerosol to remain at room temperature throughout the ion mobility analyzer.

A Keithley Regulated High Voltage Power Supply, Model 241, was employed to fix the potential between the plates. This instrument had a range of from 0 to 1000 volts. Charged aerosol particles while flowing radially outward

between the plates were subjected to a force which tended to move them toward one of the plates according to the sign of their charge. A Keithley, Model 410, Micro-Microammeter was used to measure the ion current generated by particle deposition upon the upper plate. The micro-microammeter was capable of measuring currents from 10^{-3} to 3×10^{-13} ampere. An increasing fraction of the charged particles was collected for each fixed potential difference until all the charged particles were collected.

A diagram of the experimental arrangement is given as Figure 6.

2. Experimental Results

Ion currents were recorded for each voltage applied to the ion mobility analyzer. A complete size spectrum analysis usually could be obtained in the range from 20 to 500 volts. The detailed procedure has been described in a previous report.[55] In this study, the primary interest was to find the humidity condition at which the nucleation occurred. A substantial particle size shift indicated when the droplets from a supersaturated solution converted into dry crystals. The reduction in size corresponded to a reduction in the value of V_{mean}, which is the voltage required to collect one half of the total number of particles. Therefore, V_{mean} is closely related to the count median diameter of the size spectrum. Data for sodium chloride are presented in Figure 7 as a ratio of the V_{mean} of the particles measured at the indicated humidity to the V_{mean} of dry crystals. The results show that nucleation of a fraction of the droplets was first detected when the relative humidity dipped below 48%, and that all the droplets were converted to dry crystals at about 44% relative humidity for all residence times. The data for 5 seconds residence time were taken when no residence chamber was used; the aerosal flowed directly to the ion mobility analyzer after

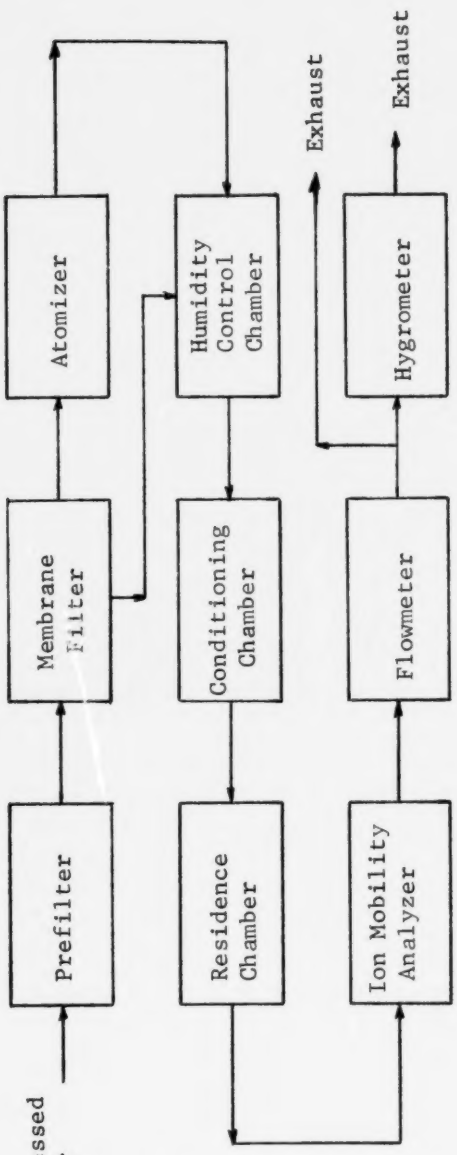

Figure 6. Diagram of the Ion Mobility Apparatus.

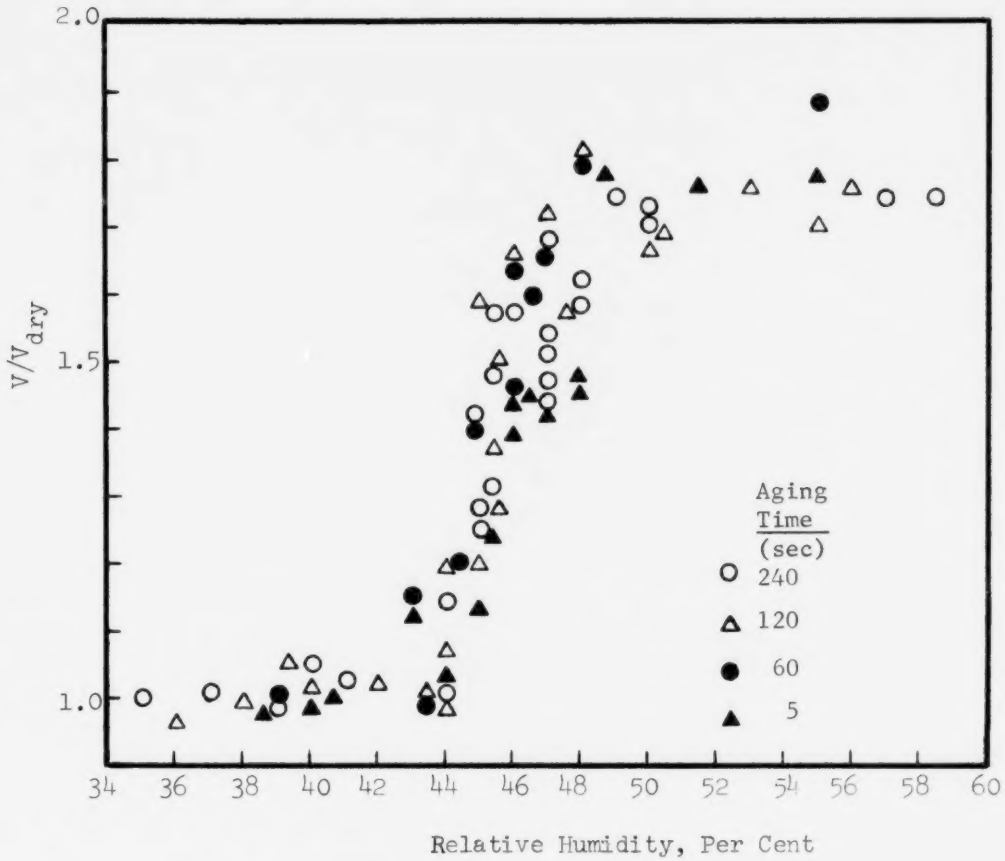

Figure 7. Experimental Ion Mobility Data for Sodium Chloride.

leaving the conditioning chamber and the copper coil. It represents the least possible aging time for the system employed. The total time including flowing through the copper coil was only about 7 seconds. The results also indicate that the nucleation process is not very sensitive to the aging time, i.e., the induction time of the nucleation process. In other words, the dependence of nucleation on induction time cannot be revealed by varying the induction time in such a small range. Several tests were made with a large chamber which permitted 1,200 seconds of aging time. No detectable difference from the small chambers was found but its use created control problems.

In general, the technique is believed satisfactory for obtaining nucleation data and its dependence on relative humidity for very fine droplets in the range between 0.01 and 0.05 μm in diameter. It is not practical, however, for obtaining data to correlate a series of induction times with nucleation phenomena.

B. Light Extinction System

It is not practical to study long nucleation induction times with a flow system. A huge chamber would be required. Control of temperature and the flow characteristic of the aerosols would make it very difficult to generate reliable data. The ion mobility technique requires a large volume of aerosol for each measurement and it is very sensitive to aerosol concentration changes during a measurement. Thus it became necessary to develop another method requiring only a small quantity of aerosol for each measurement and insensitive to the aerosol concentration. Another system was thus developed; it employed the light extinction principle.

1. General Operation and Apparatus

It was desired that light extinction data be continuously monitored

with an aerosol containing supersaturated droplets, a rapid shift in the light extinction parameter indicating the occurrence of nucleation. Unfortunately, the number of droplets gradually decreased through coagulation and settling and the shift in light extinction due to nucleation could not be distinguished from that due to coagulation and settling. After several unsuccessful attempts, a system that separates the aerosol aging and nucleation detecting was developed. Tests for aging times up to 1,800 seconds were made using continuous aerosol flow. The procedure was very similar to the ion mobility system. Tests for longer aging time were measured in a different way. The aerosol was aged in a large stainless steel chamber and a sample was taken from it periodically and examined with a light extinction measurement apparatus.

The aerosol generator was an ultrasonic nebulizer, DeVilbiss, Model 880. The larger droplets generated by the nebulizer were removed by a glass trap. The aerosol was then diluted by pre-conditioned air to the desired droplet concentration level. The relative humidity of the final aerosol was also controlled by means of this dilution air. In order to prevent nucleation from occurring in the mixing zone where the aerosol from the nebulizer met the dilution air, the latter had to be cooled so that any portion of the aerosol in the mixing zone could not have a relative humidity lower than the final relative humidity in the aging chamber. The relative humidity was determined by the dew point hygrometer, Cambridge, Model 880.

The aerosol from the aging chamber was monitored by a system consisting of a tubing heater and the light extinction measurement apparatus. The tubing heater was controlled by a foot switch. The aerosol could be heated just a few degrees above room temperature when the heater was turned on; the aerosol leaving the heater contained only dry particles in this case. The aerosol

then cooled to room temperature upon entering the light extinction measurement apparatus. The tubing heater needed to be on only about 5 seconds for each test. The light extinction measurement apparatus consisted of a 4 feet long glass tube of 13/16 inch I.D. with a light at one end and a light detector at the other. The light detector was connected to a recorder. The difference of the readings with and without the tubing heater on indicated whether or not the aerosol still contained droplets. There was no change in the recording when the aerosol contained only dry particles.

During a test the aerosol in the aging chamber was flushed from the top by an air stream of the same humidity as the aerosol entering from the bottom. The room temperature was regulated within $\pm$ 0.2^{o}F (with a huge fan and a thermostat controlled heater). Constant room temperature was essential for accurate nucleation experiments with the arrangement described.

The particle size of the dry crystals as collected by a thermal precipitation was about 0.5 $\pm$ 0.2 μm in diameter. The number concentration of the aerosol was about 10^5 particles/cm^3 and the mass concentration was about 1.5 x 10^{-5} g/ℓ. The particle loss by diffusion to the wall and by settling due to gravity could be detected by either the light extinction or by mass concentration measurements. Coagulation among particles was unavoidable, of course. Nucleation could occur when droplets collided. In view of these complications, the nucleation induction times were chosen as the point when all droplets were nucleated, i.e., the light extinction measurement became constant with and without applying heat to the aerosol. For long induction time measurements this point was determined as the midpoint of the last point at which droplets were still detected and the next point when no droplets were detected. The induction time was fairly predictable once two or three

points were accurately determined by the continuous flow method at relatively short induction times. The shortest aging time was 6 seconds; this was accomplished by bypassing the aging chamber. This point was very reproducible, and it was checked prior to every test to insure that every component of the apparatus was functioning properly. By using this as a standard, the error involved in the humidity measurement was minimized. The calibration of the hygrometer was frequently checked.

2. Experimental Results

Induction times were measured with aerosol extracted from the mixing zone to the middle of the measuring chamber. The continuous flow procedure was employed to measure induction times up to 1,800 seconds. Humidity conditions were set slightly higher than the predicted value and reduced gradually until no droplets were detected. Sufficient time was allowed for the system to achieve the steady state; it was usually several times longer than the induction time. The data were fairly reproducible. The data are presented in Figure 8. Induction times longer than 1,800 seconds were measured by the aging method. The data were predictable for induction time up to 30,000 seconds. The data for longer induction times were lower than the predicted values. This might have resulted from the severe loss of droplets during the aging period due to coagulation, settling, and wall loss. The concentration of droplets was low after long aging, and accurate detection was not possible for induction times over 30,000 seconds. The data for sodium chloride and potassium iodide are presented in Tables III and IV, respectively.

Dry crystals of sodium chloride were sampled and their size was determined from photographs made with an electron microscope to be about 0.5 μm

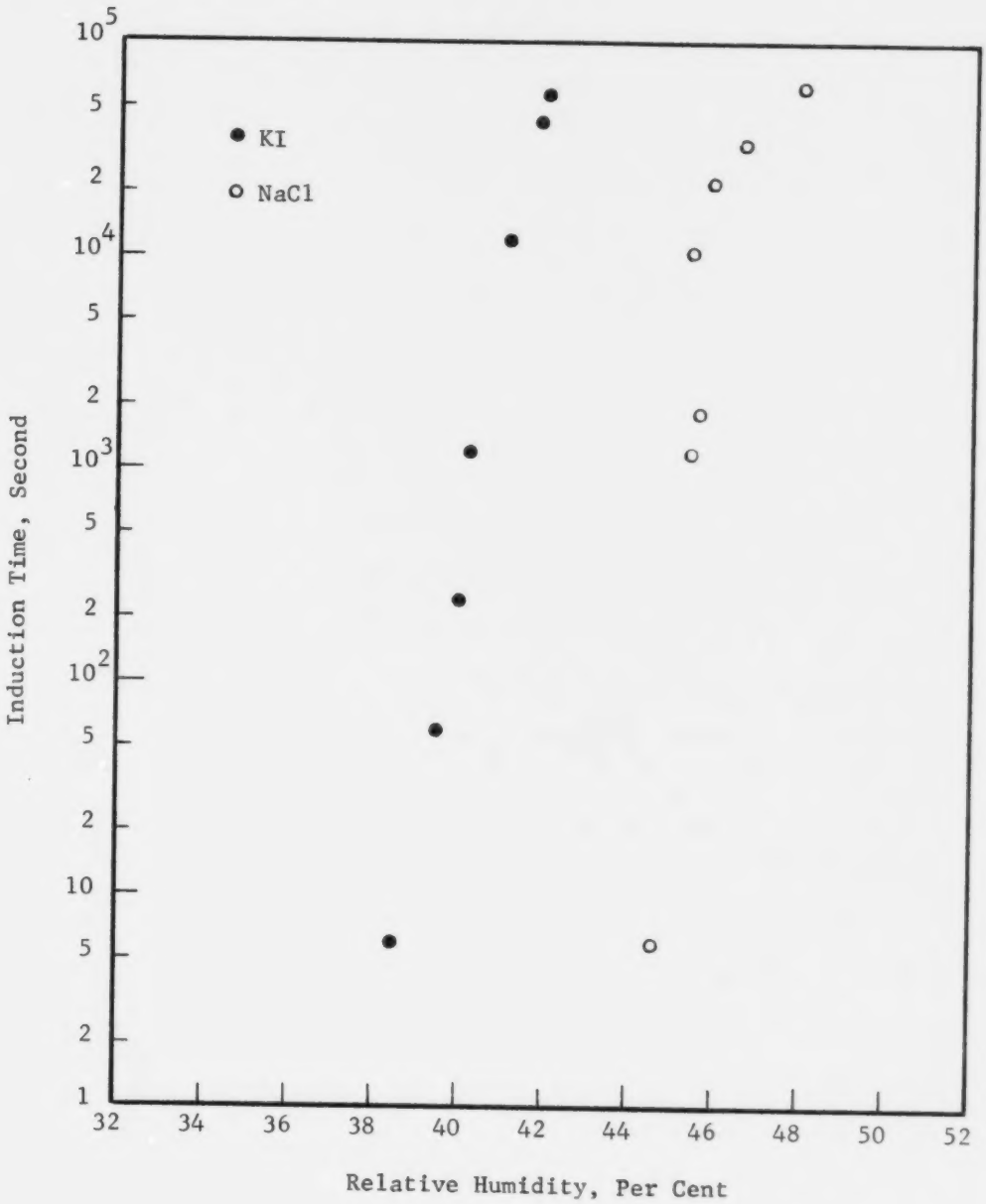

Figure 8. Induction Time Data for Airborne Droplets at Various Humidities.

TABLE III. EXPERIMENTAL DATA ON SODIUM CHLORIDE

BY LIGHT SCATTERING TECHNIQUE

Relative Humidity (%)	Induction Time (sec)	Method
44.6	6	Continuous Flow
45.4	1,200	Continuous Flow
45.6	1,800	Continuous Flow
45.4	10,500	Aging Chamber
45.9	22,500	Aging Chamber
46.6	34,200	Aging Chamber
48.0	63,000	Aging Chamber

TABLE IV. EXPERIMENTAL DATA ON POTASSIUM IODIDE

BY LIGHT SCATTERING TECHNIQUE

Relative Humidity (%)	Induction Time (sec)	Method
38.5	6	Continuous Flow
39.5	60	Continuous Flow
40.0	240	Continuous Flow
40.2	1,200	Continuous Flow
41.1	12,000	Aging Chamber
41.8	42,000	Aging Chamber
42.0	57,600	Aging Chamber

in diameter. Most of them appeared to be small cubes but some of them did not have sharp corners. The ratio of droplet size to dry crystal size was estimated from the light extinction data by assuming that the area efficiency factor was constant. Results are shown in Figure 9. These aerosols were aged only 6 seconds, and the data follow the equilibrium curve very well. This indicates that the droplets reached equilibrium very quickly as predicted from the evaporation rate.

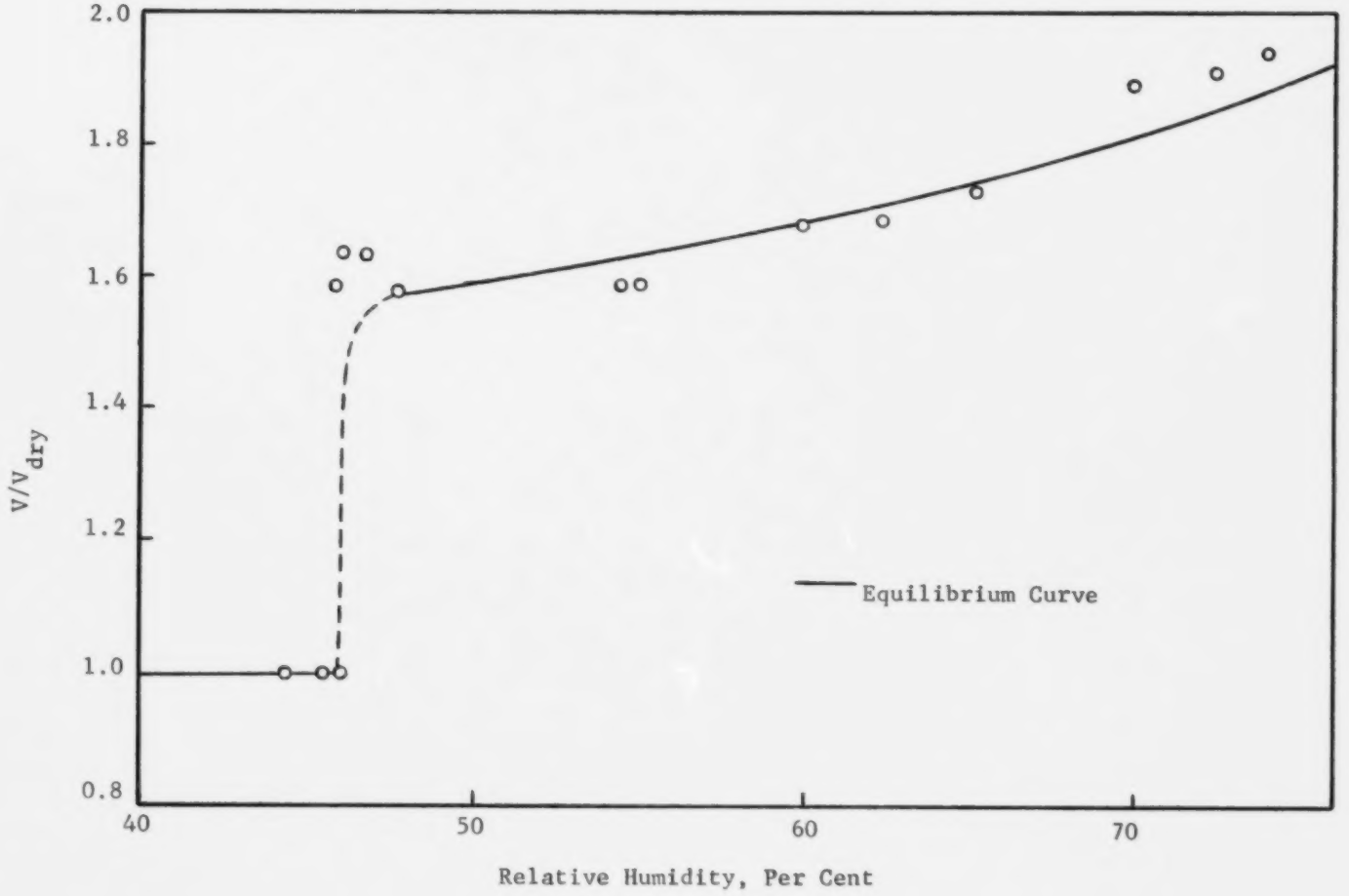

Figure 9. Experimental Light Extinction Data and Calculated Equilibrium Curve.

VI. EVALUATION OF KINETIC CONSTANT, INTERFACIAL ENERGY AND CRITICAL CLUSTER SIZE

The free energy change accompanying the formation of a cluster of radius r is expressed by

$$\Delta G(r) = 4\pi r^2\sigma + \frac{4}{3}\pi r^3 \Delta G_v \tag{20}$$

where σ is the interfacial energy of the cluster and ΔG_v the free energy change per unit volume of cluster phase. If a reference free energy level is chosen as that of the solute in the saturated solution, ΔG_v is described by

$$\Delta G_v = -\frac{kT}{\Omega} \ell n \left(\frac{a_1}{a_0}\right) \tag{21}$$

where Ω is the molecular volume given by

$$\Omega = \frac{M}{\rho N} \tag{22}$$

where M is the molecular weight of the solute, ρ the density, and N the Avogadro number.

The free energy change, ΔG, can also be expressed in terms of the number of molecules in a cluster as[2,40,42]

$$\Delta G(x) = -kTx\ell n \left(\frac{a_1}{a_0}\right) + b\, x^{2/3} \tag{23}$$

where b is given by

$$b = \sigma(4\pi)^{1/3}(3\Omega)^{2/3} \tag{24}$$

The value of ΔG goes through a maximum as r or x increases, thus the radius and the number of molecules of a critical cluster may be evaluated by

$$r^* = \frac{2\sigma M}{\rho R T \ell n \left(\frac{a_1}{a_0}\right)} \tag{25}$$

and

$$x^* = \frac{3\ 2\pi M^2 N\sigma^3}{3\rho^2 R^3 T^3 \ell n^3 \left(\frac{a_1}{a_0}\right)} \tag{26}$$

The induction time θ, which is defined in equation 13 as the time required for 99% of the droplets to go through nucleation, may thus be rewritten as

$$\ell n\ \theta = -\ \ell n \left(\frac{AV}{5}\right) + \frac{16\pi M^2 \sigma^3}{3\rho^2 R^2 T^3 k}\ \ell n^{-2} \left(\frac{a_1}{a_0}\right) \tag{27}$$

Experimental values of θ were plotted on a logarithmic grid against $\ell n^{-2}\left(\frac{a_1}{a_0}\right)$ calculated as described in Section IV for various experimental humidities. The results are presented in Figures 10 and 11. The kinetic constants were calculated from the intersections of the straight lines at $\ell n^{-2}\left(\frac{a_1}{a_0}\right) = 0$. The interfacial energies were evaluated from the slopes of the straight lines. The values and units of the parameters and constants used in the calculations are presented in Table V.

The kinetic constants of sodium chloride and potassium iodide solutions are determined to be 10^{48} and 10^{41} $cm^{-3} sec^{-1}$, respectively. These

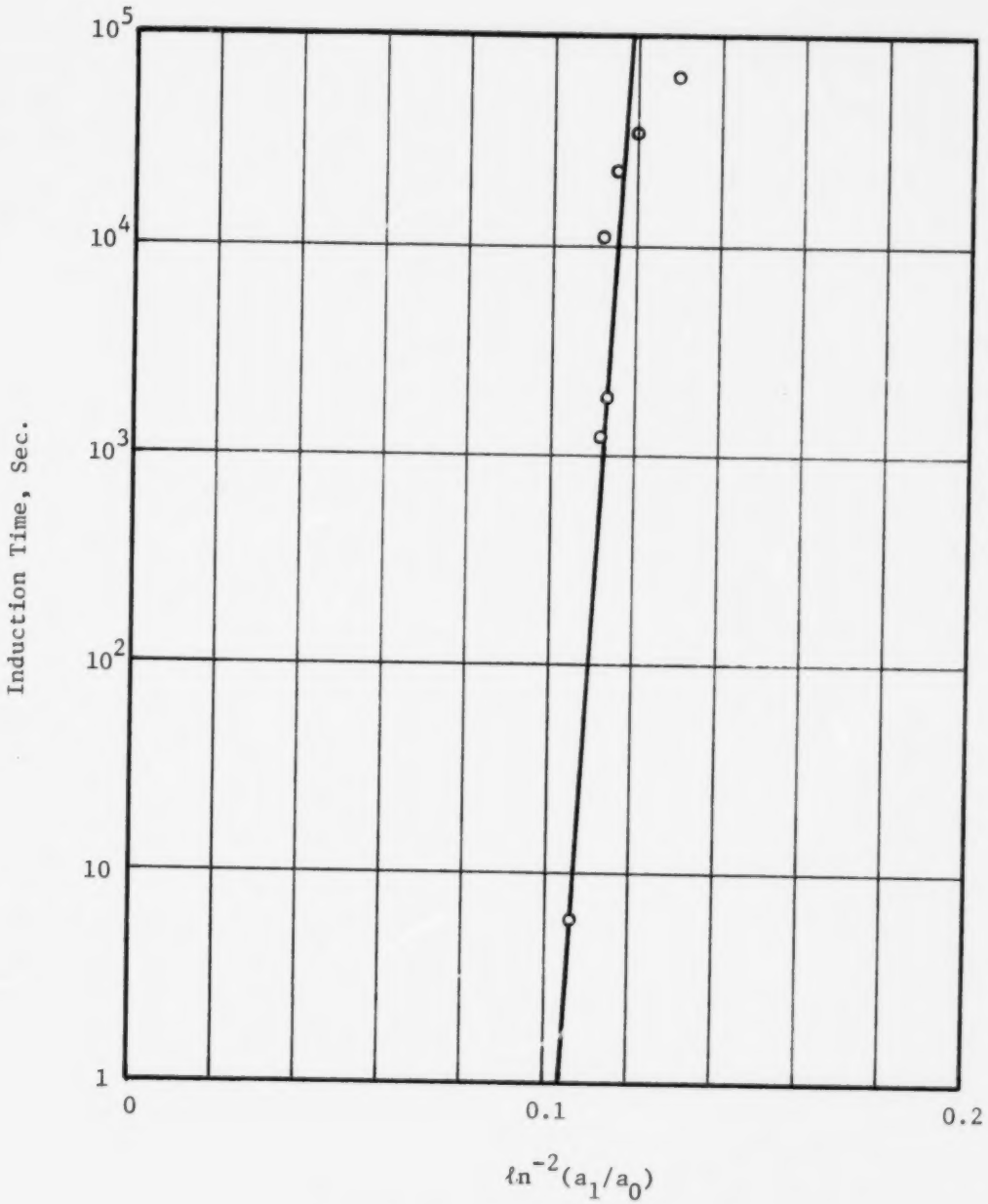

Figure 10. Induction Time of Aqueous Sodium Chloride Droplets as a Function of $Ln^{-2}(a_1/a_0)$.

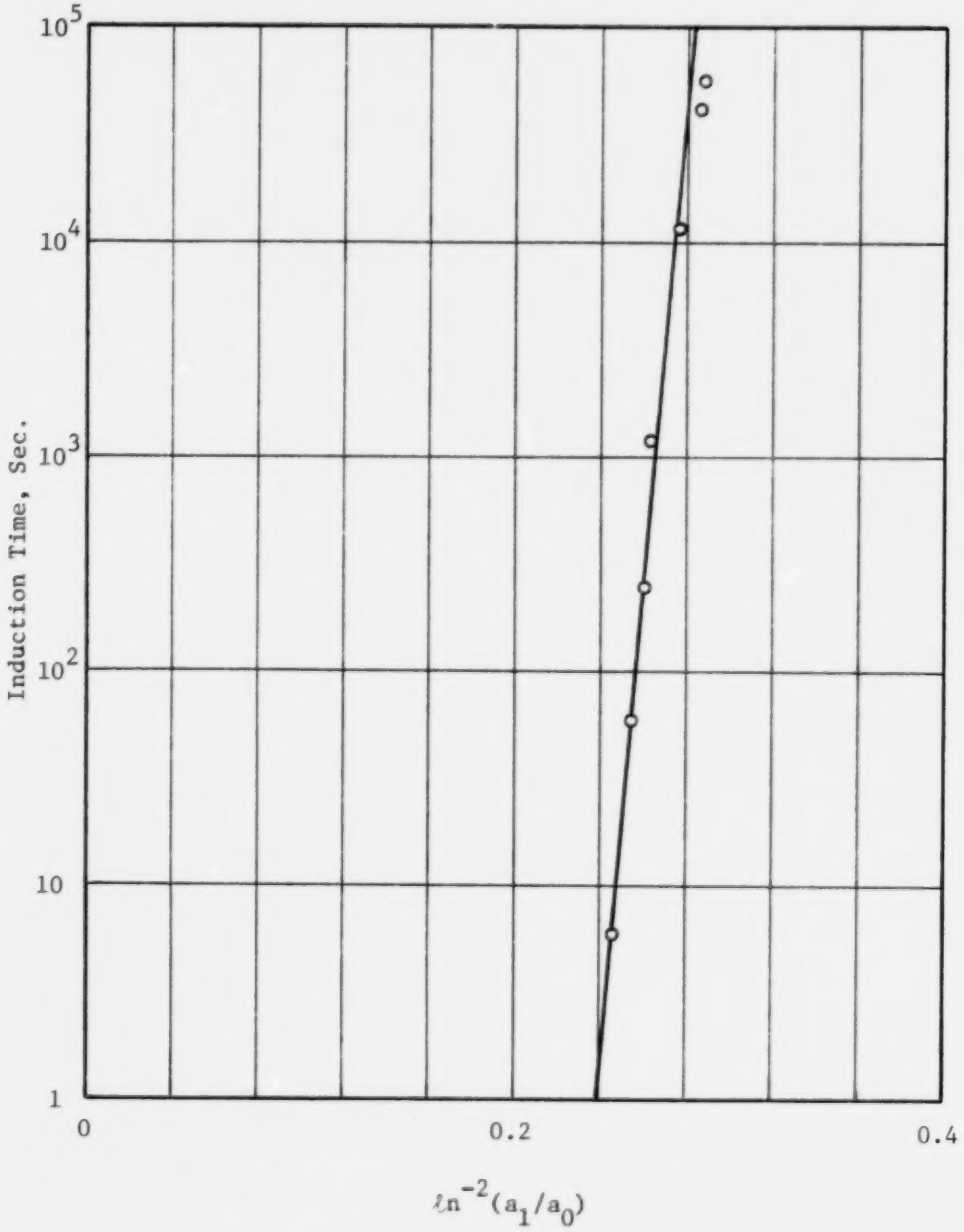

Figure 11. Induction Time of Aqueous Potassium Iodide Droplets as a Function of $Ln^{-2}(a_1/a_0)$.

TABLE V. PARAMETERS AND CONSTANTS USED IN THE CALCULATION OF KINETIC CONSTANT AND INTERFACIAL ENERGY

Symbol	Name	Value	
k	Boltzmann Constant	1.3805×10^{-16} erg $^{o}K^{-1}$	
R	Gas Constant	8.31432×10^{7} erg $^{o}K^{-1}mole^{-1}$	
N	Avogadro Number	6.0226×10^{23} $mole^{-1}$	
		NaCl	KI
ρ	Density	2.165 g cm^{-3}	3.13 g cm^{-3}
M	Molecular Weight	58.44 g $mole^{-1}$	166.01 g $mole^{-1}$
V	Volume of a Droplet	5×10^{-14} cm^{3}	5×10^{-14} cm^{3}

experimental values seem to be reasonable when compared with theoretical values, although a critical discussion is not possible at this time due to the uncertainties in the theory. The kinetic constant A has always been at the center of uncertainty in nucleation theory. The values calculated from classical nucleation theory lie in the range 10^{33} to 10^{35}. An additional contribution of 10^{17} has been suggested by Lothe and Pound from their statistical mechanical revisions.[2]

Interfacial energies of sodium chloride and potassium iodide calculated from the experimental data are, respectively, 115.9 and 51.6 ergs cm^{-2}. The interfacial free energy of sodium chloride is 12.9 ergs cm^{-2} in supersaturated aqueous solution according to Hidalgo.[54] The value is much too low when compared to the minimum value given by Burke and Ubbelohde,[58,59,60] 36.7 ergs cm^{-2}, for the liquid-solid molten system. It is believed that a heater used in Hidalgo's measuring device caused at least a large part of this discrepancy. The experimental interfacial energy measured for sodium chloride crystals in a melt has been reported[60] to be 84.1 ergs cm^{-2}. The surface tension at the melting point[60] as extrapolated from experimental data for sodium chloride at temperatures above the melting point is 125.2 ergs cm^{-2}. This value represents the interfacial energy of the liquid-gas interface. It is expected from structure considerations that the interfacial energy of the solid-solution interface should fall between these two values. Therefore, the value of 115.9 ergs cm^{-2} for sodium chloride in solution seems to be reasonable. The homogeneous nucleation of aqueous sodium chloride solution has not been studied by any other methods so far as is known mainly due to its very small temperature coefficient of solubility. A critical comparison of this measured

value to others is not possible at this time.

The interfacial energy of potassium iodide as measured here, 51.6 ergs cm^{-2}, also falls in between the values[60] for the solid-melt system, 47.2 ergs cm^{-2}, and the melt-gas system, 87.6 ergs cm^{-2}. The concentration of aqueous potassium iodide at which nucleation takes place is much higher than for sodium chloride solutions. This may explain why the measured interfacial energy for potassium iodide solution is much closer to the solid-melt value than for sodium chloride. From the structure point of view, the difference in properties between the solution and the crystal are smaller when the concentration of the solute is higher. The minimum interfacial energy can be assumed to be that for the solid-melt system. It must be pointed out that the concentration required to accomplish nucleation in a given time is not controlled by the experimental system but by the properties of the substances.

The critical cluster sizes in terms of the number of molecules and free energy values at various supersaturations are calculated from the experimental data and are presented in Tables VI and VII for sodium chloride and potassium iodide.

Experimental data measured by cooling a solution in a container are considered to relate to heterogeneous nucleation. The data vary from system to system and the effects of the container wall cannot be avoided. The general characteristics of heterogeneous nucleation data suggest low kinetic constants and interfacial energies. For example, the kinetic constants reported are as low as 10^1 to 10^4 for aqueous solutions of metal halides.[61] The interfacial energies reported for sodium chloride and potassium iodide solutions are 3.53 and 0.83 ergs cm^{-2}, respectively.[93]

TABLE VI. PROPERTIES OF CRITICAL CLUSTERS ON SODIUM CHLORIDE IN AQUEOUS SOLUTIONS

Solution Concentration (molality)	x^* (number of molecules)	$\Delta G(x^*)$ (10^{-12} erg)	$-\frac{\Delta G(x^*)}{2.303\ kT}$
10.00	240	9.230	98.08
10.50	177	7.529	80.00
11.00	137	6.348	67.45
11.50	110	5.492	58.36
12.00	90	4.807	51.08
12.50	76	4.296	45.65
13.00	65	3.879	41.22
13.50	57	3.542	37.64
14.00	51	3.274	34.79
14.50	46	3.050	32.41
15.00	42	2.863	30.42

TABLE VII. PROPERTIES OF CRITICAL CLUSTERS ON POTASSIUM IODIDE IN AQUEOUS SOLUTIONS

Solution Concentration (molality)	x^* (number of molecules)	$\Delta G(x^*)$ (10^{-12} erg.)	$-\frac{\Delta G(x^*)}{2.302\ kT}$
20.00	128	4.190	44.52
22.00	107	3.721	39.54
24.00	94	3.413	36.27
26.00	86	3.199	33.99
28.00	79	3.026	32.15
30.00	74	2.891	30.72
32.00	70	2.791	29.66
34.00	67	2.705	28.74
36.00	64	2.641	28.06
38.00	62	2.582	27.44
40.00	60	2.525	26.83

In addition to the system wall, impurity particles in the bulk solution also induce heterogeneous effects into the nucleation. Heterogeneous nucleation always takes place at relatively low supersaturations; its magnitude is controlled by the experimental systems. It is doubtful that homogeneous nucleation can ever be studied in a bulk solution system.

The extrapolation of the relative humidity curve for potassium iodide to high supersaturations as shown in Figure 2 introduces an uncertainty as discussed in Chapter IV. The magnitude of the uncertainty involved in the extrapolation is demonstrated by the pair of additional curves shown in Figure 2. The kinetic constants and the interfacial energies evaluated from each of these three curves are presented in Table VIII. The solution molalities in equilibrium to 40% relative humidity given in Table VTII. demonstrate the magnitudes of the difference among the three extrapolations. The values of the kinetic constant and the interfacial energy given in Table VIII indicate that, if the actual solution molality at a given humidity condition is smaller than the extrapolation curve, the KI data would show less error. The error caused by the extrapolation procedure for the interfacial energy is small in all cases, however.

TABLE VIII. KINETIC CONSTANTS AND INTERFACIAL ENERGIES OF POTASSIUM IODIDE EVALUATED FROM DIFFERENT EXTRAPOLATIONS IN FIGURE 2.

	Curve KI(L)	Curve KI	Curve KI(H)
Kinetic Constant, $cm^{-3} sec^{-1}$	10^{39}	10^{41}	10^{48}
Interfacial Energy, erg cm^{-2}	51.5	51.6	53.5
Solution Molality in Equilibrium at 40% Relative Humidity	27	32	42

VII. EFFECTS OF SURFACES ON NUCLEATION OF SOLUTIONS

Heterogeneous nucleation occurs at lower degrees of supersaturation than does homogeneous nucleation. It is also true that the induction time--the time from the creation of the supersaturated state to the appearance of crystals--is shorter in the presence of foreign surfaces. The exact nature of these phenomena is not well understood and occasionally surface effects are underestimated in homogeneous nucleation studies. The following suggests a method for investigating the magnitude of surface effects by means of a droplet technique. Basically, it involves supporting droplets on various surfaces such as spider silk,[56,57] glass fiber, glass plate, and treated glass surfaces and detecting the appearance of crystals in the droplets through microscopic observation.

A. Experimental Apparatus and Procedures

Aqueous solutions of sodium chloride and potassium iodide were employed in this investigation. A solution was atomized into a stream of droplets and a few droplets were caught by the surface of study. This sample was then placed in a chamber which was mounted on the stage of an optical microscope. Two air streams, one dry and the other made humid by bubbling through two water columns in series, were proportionally mixed to yield the desired humidity. The dew point of the mixed stream was continuously monitored by a Cambridge hygrometer, Model 880. The dew point could be maintained within $\pm$ 0.2°F without further adjustment once conditions were established. The air stream was kept at room temperature which was itself maintained very nearly constant. To start a test, the humid air was led to the observation chamber until all dry crystals became droplets. Then air of a predetermined low humidity was introduced at a flow rate of 0.5 ℓ/min. The droplets

evaporated to reach an equilibrium size very quickly, generally in a few seconds, the length of time depending on the air humidity. The time for the droplet to reach the equilibrium supersaturation was always very short compared to the induction time. Induction time recording was started when evaporation apparently ceased. This equilibrium condition was somewhat difficult to pin-point accurately; repeated tests minimized the error. Induction time was considered ended when a crystal first appeared in the droplet; this point was quite reproducible. Data reported in this study are for crystal size of about 30 μm. The same crystal was used repeatedly to obtain the data at various humidity conditions for a particular surface. It was found that induction times up to several hundred seconds were the same for all droplets observed. They varied some for very long measurements among different droplets but the differences were small compared to the induction time even when their sizes were not the same. A glass cylinder containing $CuSO_4$ solution was placed between the microscope illuminator and the observation chamber to remove much of the heat in the light. The illuminator was set at low intensity and was usually turned off during a long test until a check was needed. The induction period could be predicted very closely by extrapolation of experimental data measured at shorter times so it was not necessary to leave the illuminor on all the time except for short runs. No temperature change in the observation chamber was detected when the illuminator was turned on, however.

B. Nucleation of Droplets on Threads

Threads such as spider silk and glass wool were employed to support the droplets for nucleation study. The spider silk was approximately 3 μ in diameter and very uniform. It was mounted on a steel-wire frame and cleaned

in an ultrasonic water bath to remove water-soluble substances. After drying, solution droplets were placed on the silk by directing fine atomized droplets toward it. The droplets generally were converted to dry crystals before they were placed in the observation chamber since the room air was usually dry enough to induce nucleation. Humid air was first let into the observation chamber, condensing on and dissolving the crystals on the spider silk into droplets. Neighboring droplets sometimes joined together to form larger droplets. Only one droplet was needed for study, however. Sometimes two or more droplets could be seen within one view. The induction periods were almost the same for all of them even when their sizes were quite different.

The diameter of the glass threads was about 10 μm and not as uniform as the spider silk. A smooth and uniform section was chosen for use; the procedure was similar to that for the spider silk.

Multiple crystals were created in one droplet upon rapid evaporation in relatively dry air; in other words, when the induction time was short. However, a single cubic crystal could be obtained by letting the droplets evaporate slowly in air of relatively high humidity. The data for sodium chloride droplets on spider silk are presented in Table IX. Many values are average values from at least three tests although deviations were very small. Induction times for sodium chloride droplets on glass thread were longer than those on the spider silk at the same conditions. These results are given in Table X. The data for sodium chloride are plotted against supersaturation ratio and are presented in Figure 12. The results for potassium iodide on spider silk are given in Table XI and are also shown in Figure 13. The induction times are much shorter than are those of sodium chloride at the

TABLE IX. NUCLEATION DATA FOR AQUEOUS SODIUM CHLORIDE DROPLETS ON SPIDER SILK

Relative Humidity (%)	Concentration (molality)	Supersaturation Ratio	Induction Time (sec)
47.6	12.80	2.075	2.4
48.4	12.54	2.032	2.9
48.6	12.47	2.021	3.0
52.1	11.44	1.854	5.5
52.8	11.24	1.822	6.5
54.3	10.84	1.757	9.8
56.0	10.40	1.686	12.0
57.0	10.16	1.647	16.5
57.6	10.01	1.622	20.0
58.1	9.90	1.605	21.5
58.4	9.82	1.592	23.0
61.2	9.17	1.486	42.0
63.0	8.75	1.418	68.0
63.9	8.54	1.384	110.0
64.2	8.45	1.370	135.0
64.8	8.33	1.350	200.0
65.4	8.20	1.329	260.0
66.4	7.98	1.293	450.0
66.8	7.90	1.280	540.0
68.1	7.62	1.235	1950.0
68.4	7.57	1.227	2650.0
68.9	7.48	1.212	4600.0
69.2	7.40	1.199	7800.0

TABLE X. NUCLEATION DATA FOR AQUEOUS SODIUM CHLORIDE DROPLETS ON GLASS THREAD

Relative Humidity (%)	Concentration (molality)	Supersaturation Ratio	Induction Time (sec)
46.3	13.24	2.146	3
49.0	12.35	1.998	6
50.3	11.97	1.937	8
54.0	10.92	1.767	16
55.7	10.48	1.696	23
56.2	10.35	1.675	27
58.5	9.80	1.586	70
61.0	9.20	1.489	350
64.3	8.45	1.367	2500
65.8	8.10	1.311	7500

TABLE XI. NUCLEATION DATA FOR AQUEOUS POTASSIUM IODIDE DROPLETS ON SPIDER SILK

Relative Humidity (%)	Concentration (molality)	Supersaturation Ratio	Induction Time (sec)
58.6	12.36	1.394	3
59.4	12.08	1.361	4
60.7	11.53	1.300	8
61.5	11.22	1.267	14
62.1	11.00	1.240	21
62.3	10.92	1.232	28
63.1	10.65	1.201	60
63.3	10.58	1.192	72
63.6	10.47	1.180	125
63.8	10.40	1.173	170
64.3	10.22	1.153	540
64.8	10.06	1.135	1450
65.0	10.00	1.129	3200

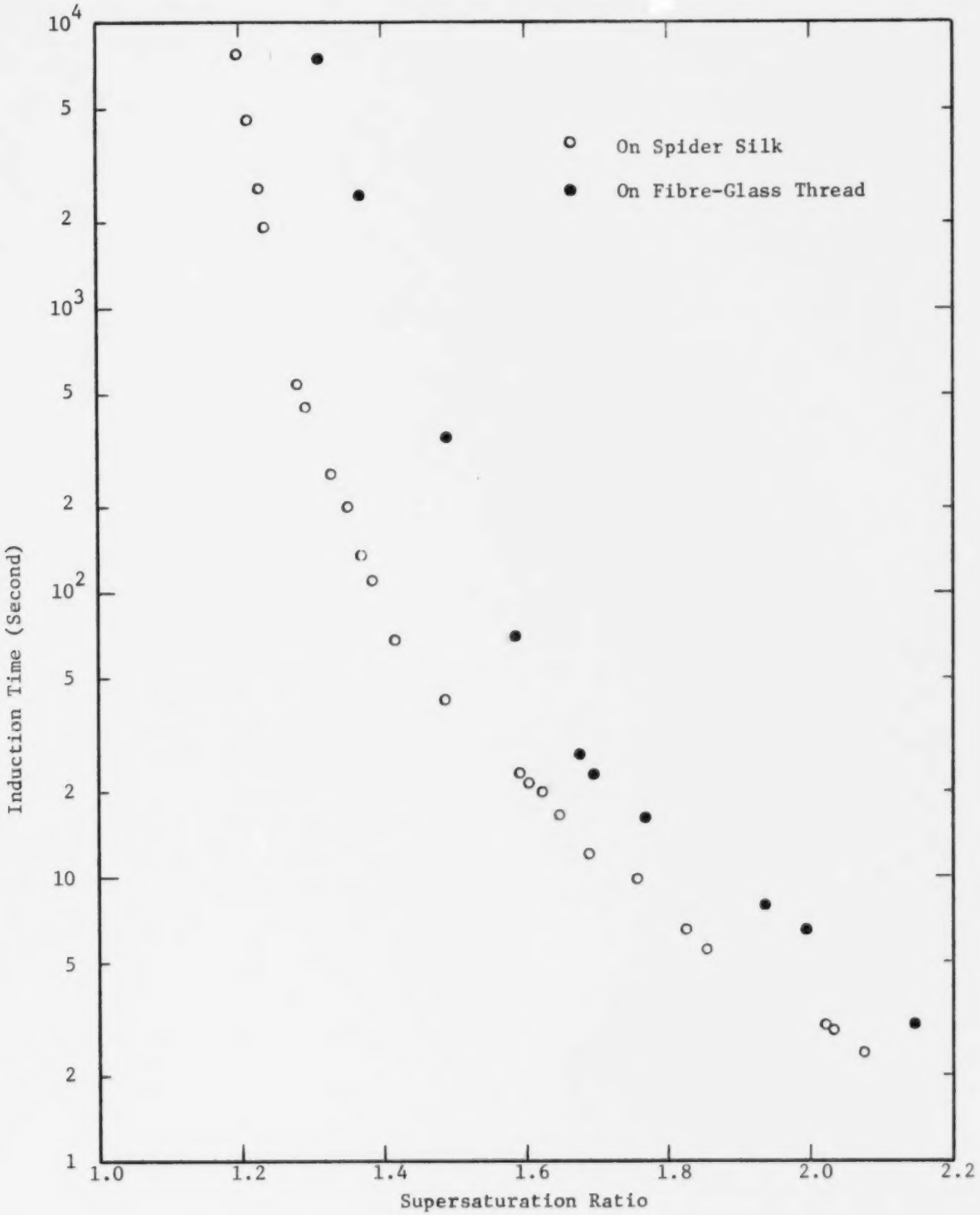

Figure 12. Induction Time of Aqueous Sodium Chloride Droplets on Threads.

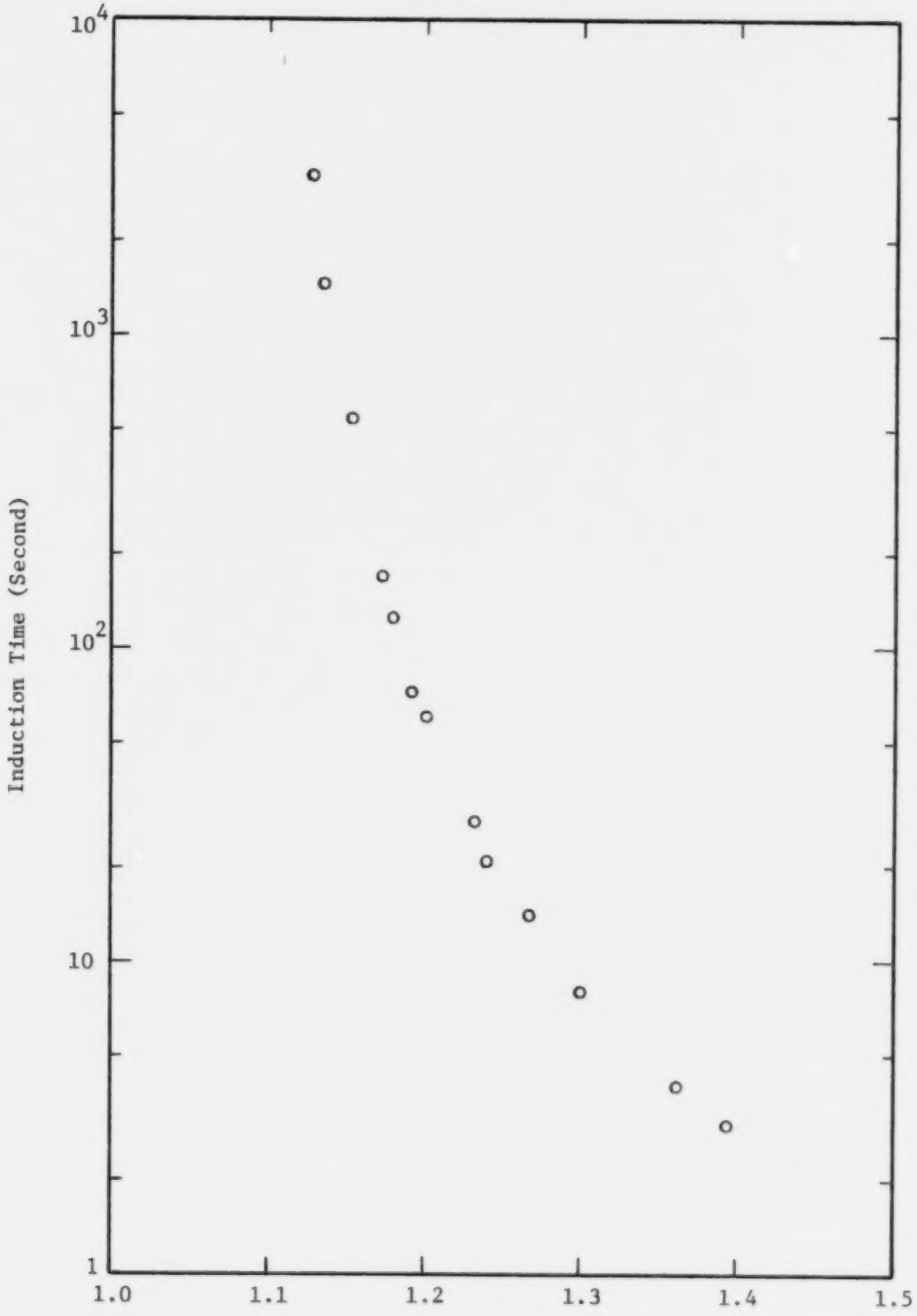

Figure 13. Induction Time of Aqueous Potassium Iodide Droplets on Spider Silk.

same supersaturation.

One droplet on the spider silk containing an insoluble particle was also examined. No significant difference from a pure solution droplet was detected. Apparently the effect of the thread surface on nucleation induction time is much greater than that of an insoluble particle within the droplet and dominates the nucleation process in this case. The insoluble particle in the droplet was about 10 μm in diameter; it was expelled to the surface of the crystal by the crystallization process.

Induction times for droplets at various locations of the threads were almost identical. This suggests that the surface of the threads was quite uniform in nature. When only one crystal was formed in a droplet, its formation was always initiated near where droplet and thread came into contact and surface curvature reversed, which resulted from the surface tension of the solution and the capillary force between the solution and the thread surface. Multiple crystals were formed when supersaturation was very high and the induction time short. In this case a number of crystals were formed at equally spaced intervals along the surface of the thread. Apparently, capillary (contact) forces play an important role. They cause the droplet to extend along the thread surface to form a tip where the surface area-to-liquid volume ratio is higher than for other parts of the droplet. The equilibrium concentration of the solution near the tip is apparently achieved ahead of the body of the droplet during the initiation period. The capillary force and surface tension exert a strain on the liquid around the tip which may also alter the nucleation characteristics. There is a possibility that a higher supersaturation is created locally in this area due to either or both the surface curvature and the capillary force.

At low supersaturation conditions, the presence of the first critical nucleus and the growth of this nucleus that immediately follows reduces the supersaturation of the solution elsewhere in the droplet thus preventing further formation of critical nuclei. Thus only one crystal is formed. The nucleation rate is high under high supersaturation conditions. Many critical nuclei are formed at almost the same time. Multiple nucleation is initiated elsewhere before the effect of the growth of the first crystal is registered. These explanations seem to satisfy all the observations even though satisfactory theoretical explanations of this type of heterogeneous nucleation are still not available.

Another observation is also worth mentioning. It is that droplets completely surrounding the thread nucleate at the same time as those attached only to the surface of the thread. The influence of surfaces on the nucleation process for both cases seems to be identical.

C. Nucleation of Droplets on Flat Surfaces

Microscope slides were employed here. They were washed and rinsed with distilled water prior to use. Some of them were then covered with a thin film of vacuum grease (Apiezon Grease) while others were covered with a thin film of silicone fluid (Dow Corning 200). Droplets of solutions were sprayed onto them as described above for the study of droplets on threads. The experimental data for sodium chloride droplets on the clean, the vacuum-grease coated, and the silicone coated glass surfaces are presented in Tables XII, XIII, and XIV, respectively. The experimental results with sodium chloride are also presented in Figure 14. Droplets on a clean glass surface required a much shorter time to nucleate than on surfaces covered with either a thin film of vacuum grease or silicone oil. Interfacial characteristics such as contact angles among the solution

TABLE XII. NUCLEATION DATA FOR AQUEOUS SODIUM CHLORIDE DROPLETS ON CLEAN GLASS SURFACE

Relative Humidity (%)	Concentration (molality)	Supersaturation Ratio	Induction Time (sec)
46.4	13.20	2.139	6
49.2	12.30	1.994	10
50.5	11.90	1.929	20
50.9	11.80	1.912	28
52.2	11.35	1.840	60
53.5	11.06	1.793	130
54.4	10.81	1.752	315
55.3	10.67	1.729	1400
56.8	10.20	1.653	5500

TABLE XIII. NUCLEATION DATA FOR AQUEOUS SODIUM CHLORIDE DROPLETS ON GLASS SURFACE COATED WITH APIEZON GREASE

Relative Humidity (%)	Concentration (molality)	Supersaturation Ratio	Induction Time (sec)
46.2	13.25	2.144	7
49.0	12.35	1.998	12
49.6	12.22	1.977	22
50.6	11.90	1.926	70
51.1	11.72	1.896	320
52.0	11.47	1.856	1400
53.6	11.02	1.783	8200

TABLE XIV. NUCLEATION DATA FOR AQUEOUS SODIUM CHLORIDE DROPLETS ON GLASS SURFACE COATED WITH DOW CORNING 200 SILICONE FLUID (A Dimethylpolysiloxane)

Relative Humidity (%)	Concentration (molality)	Supersaturation Ratio	Induction Time (sec)
43.5	14.25	2.306	7
43.8	14.12	2.288	8
46.6	13.15	2.128	22
47.2	12.94	2.094	30
47.6	12.80	2.071	37
48.0	12.66	2.049	56
48.2	12.60	2.039	54
48.8	12.42	2.010	100
49.5	12.21	1.976	170
50.6	11.86	1.919	950
51.3	11.68	1.890	6750

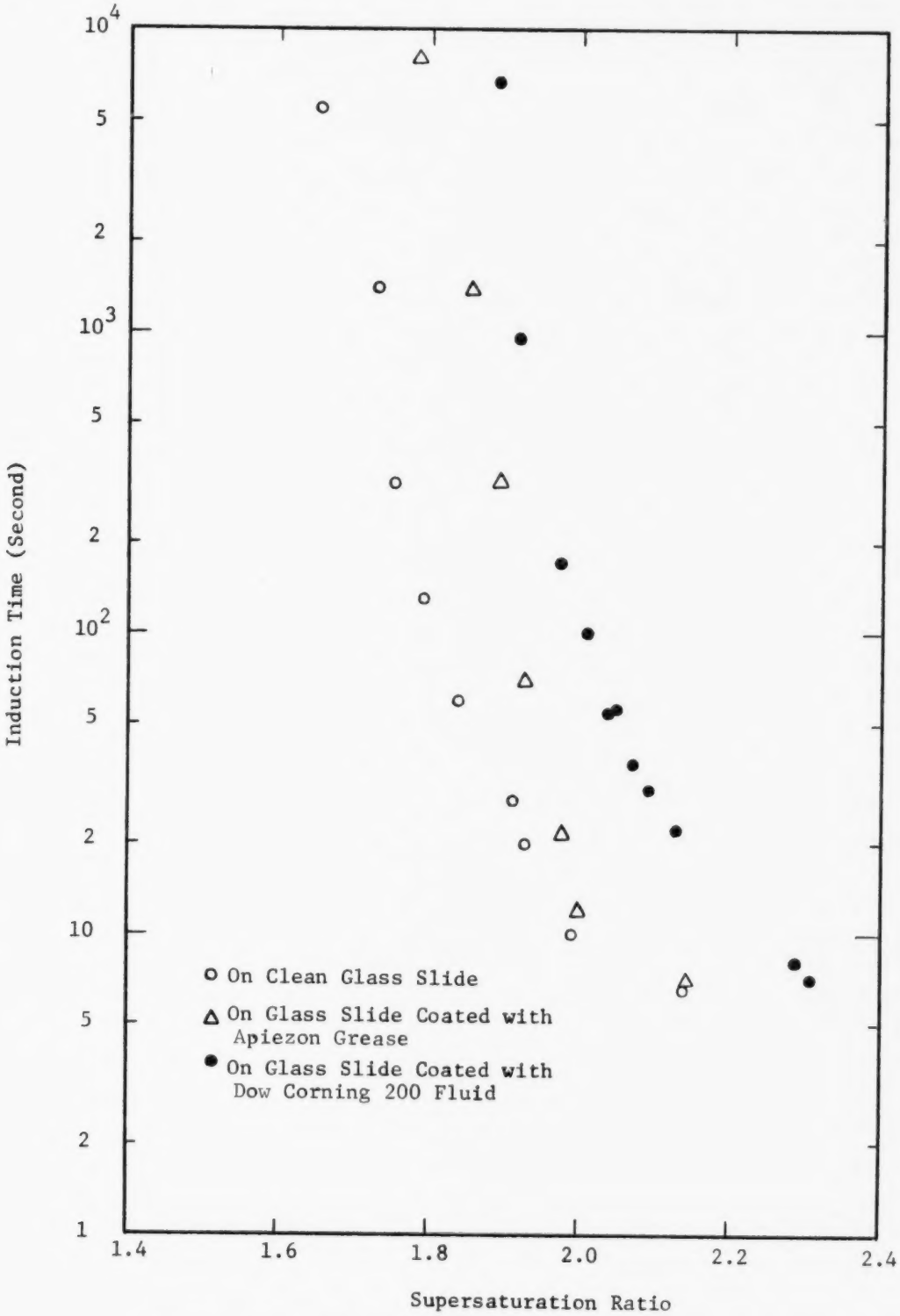

Figure 14. Induction Time of Aqueous Sodium Chloride Droplets on Flat Surfaces.

droplets and the various surfaces are not identified. As would be expected, the data indicate that surfaces of poor wettability have less effect on the nucleation droplets placed on them.

D. Theoretical Considerations and Discussion

The nucleation mechanism of a droplet supported on a surface is quite different from that of an airborne droplet. Experimental observations show that all droplets on the same surface nucleate at essentially the same time regardless of their size. No theories available at this time fully explain these observations. An attempt is made here to describe the mechanism. It is highly speculative because the validity of some of the assumptions has not been tested.

Nucleation on surfaces from solution is very similar to crystal growth even though the surface material is different from the solute. The free energy change accompanying the growth of a cluster on a supporting surface is greater than that accompanying the growth of a crystal. The total free energy change accompanying the formation of a cluster on a surface may be expressed by

$$\Delta G_S = A_1 \sigma_{SL} + A_2 \sigma_{SS} + f(\phi) + V_c \Delta G_v \qquad (28)$$

where A_1 and A_2 are the surface areas of the cluster in contact with the solution and the supporting surface, respectively; σ_{SL} and σ_{SS} the interfacial energies of the cluster in the solution and at the surface interface, respectively; $f(\phi)$ an energy term associated with the contact angle between the cluster and the surface, V_c the volume of the ciuster, and ΔG_v the free energy change per unit volume of the cluster phase.

The supporting surface in contact with the solution is assumed to contain adsorbed monomers. The monomers are mobile and they diffuse along the surface. The mean distance that monomers travel on the surface before being desorbed depends on the solution and the surface. The growth of a cluster is assumed to be controlled by two processes. The cluster attains monomers through the diffusion process on the surface. The rate, $R_1(x)$ of gaining monomers is proportional to the cluster size and the properties of the adsorbed monomer. The cluster also releases molecules to the solution because of a relationship between the free energy and cluster size in the post-critical region. This rate, $R_2(x)$, is also proportional to cluster size. The growth rate of the cluster is the difference of these two processes. The growth rate of the cluster is thus expressed by

$$\frac{dx}{dt} = R_1(x) - R_2(x) \tag{29}$$

and

$$t^* = \int_1^{x^*} \frac{dx}{R_1(x) - R_2(x)} \tag{30}$$

where t^* is the time required for a critical nucleus containing x^* monomers to form. The diffusion characteristics of the adsorbed monomers on the surface and the shape of the cluster are not known. Thus $R_1(x)$ and $R_2(x)$ cannot be evaluated. $R_1(x)$ should always be greater than $R_2(x)$ when $x < x^*$ so that nucleation can occur. $R_1(x)$ is proportional to the degree of supersaturation of the solution, while $R_2(x)$ is inversely proportional to the degree of supersaturation of the solution. The critical cluster size, furthermore, is inversely proportional to the degree of supersaturation of

the solution. In view of these characteristics, $R_2(x)$ may overtake $R_1(x)$ before the cluster size reaches a critical value at low supersaturation. Nucleation would not occur in this case. The degree of supersaturation at which this phenomenon would occur, of course, varies with the supporting surface, since $R_1(x)$ is strongly dependent on the characteristics of the surface in addition to the properties of the solute. For example, it takes 2 min. for a sodium chloride droplet to nucleate at a supersaturation ratio of 1.8 on a clean glass surface. It takes about 2 hrs. for a droplet of the same concentration to nucleate on an Apiezon grease-coated glass surface. A droplet having the same concentration will not nucleate in a day on a silicone-coated glass surface. It is very doubtful if a droplet would ever nucleate on the silicone surface if the supersaturation of 1.8 were further reduced. This can be seen from Figure 14.

If $R_1(x)$ and $R_2(x)$ vary only with the cluster size after a droplet on a surface reaches the equilibrium state, the induction time t^* should be a fixed value. The induction time thus becomes identical for all droplets of the same kind regardless of any difference in size since $R_1(x)$ and $R_2(x)$ are not functions of the droplet size provided the concentration is not related to size.

Since a rigorous expression of the induction time is not possible at this time, the following simple relation is proposed

$$t^* = \frac{1}{B \exp\left[- \frac{\Delta G_S^*}{kT} \right]} \tag{31}$$

where B is the heterogeneous kinetic constant and ΔG_S^* the free energy accompanying the formation of the critical nucleus on the surface. The critical cluster size x^* may be evaluated from equation 28 by letting $\partial(\Delta G_S^*)\partial x = 0$. The term ΔG_S^* may be expressed by inserting x^* into equation 28 as

$$\Delta G_S^* = A_1^* \sigma_{SL} + A_2^* \sigma_{SS} + f(\phi)^* + V_c^* \Delta G_v \tag{32}$$

where the superscript * indicates a critical cluster. Since the shape of the critical nucleus and the diffusion characteristics of the monomers on the surface are not known, the critical properties in equation 32 cannot be evaluated. However, if $f(\phi)^*$ is negligible for a crystalline phase, equation 32 may be approximated by

$$\Delta G_S^* = C' \ell_n^{-2}\left(\frac{a_1}{a_0}\right) \tag{33}$$

where C' is a function of the geometry of the critical nucleus, the properties of the supporting surface, and the surface energies σ_{SL} and σ_{SS}.

Equation 31 may be rewritten as

$$\ell n\ t^* = -\ell n\ B + C\ \ell n^{-2}\left(\frac{a_1}{a_0}\right) \tag{34}$$

where B and C are constants for the same surface and solute.

Experimental data for aqueous sodium chloride droplets on various surfaces are presented in Figure 15. The factors B and C for each surface are presented in Table XV. The equivalent values for airborne droplets are also included for comparison.

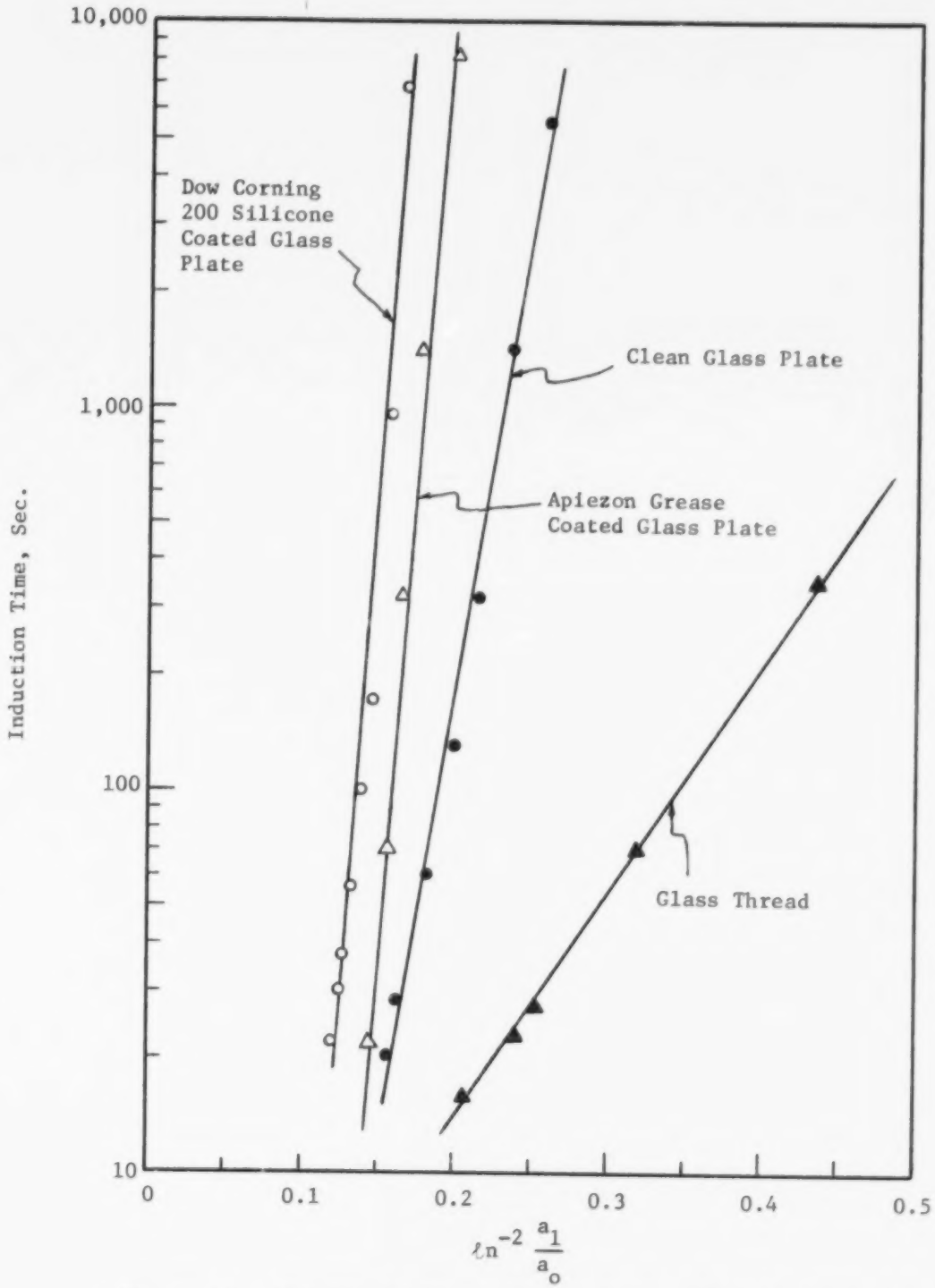

Figure 15. Induction Time of Aqueous Sodium Chloride Droplets on Various Surfaces as a Function of $Ln^{-2}(a_1/a_0)$

TABLE XV. HETEROGENEOUS NUCLEATION FACTORS FOR AQUEOUS SODIUM CHLORIDE DROPLETS ON VARIOUS SURFACES

Surface	B (sec^{-1})	C
Glass Thread	$10^{0.029}$	13.5
Clean Glass Plate	$10^{2.5}$	54.8
Apiezon Grease Coated Glass Plate	$10^{6.3}$	119.1
Dow Corning 200 Silicone Coated Glass Plate	$10^{5.6}$	130.3
Airborne Droplets*	-	768

*Homogeneous Nucleation

Experimental data for aqueous sodium chloride droplets on spider silk are presented in Figure 16. The data cover a wide range of supersaturations. Three zones are observed, each zone giving a straight line as shown in Figure 16. The factors B and C for each zone are given in Table XVI. The explanation of the development of zones may be found in a change in cluster geometry. The number of monomers in a critical cluster is approximately proportional to $\ell n^{-3}(a_1/a_0)$. As the number of monomers in a cluster increases, it is understandable that the shape may change. Therefore, equation 34 may apply only to data obtained in a relatively narrow range as shown in Figure 15. The induction time measured at $\ell n^{-2}(a_1/a_0) = 0.72$ indicates that

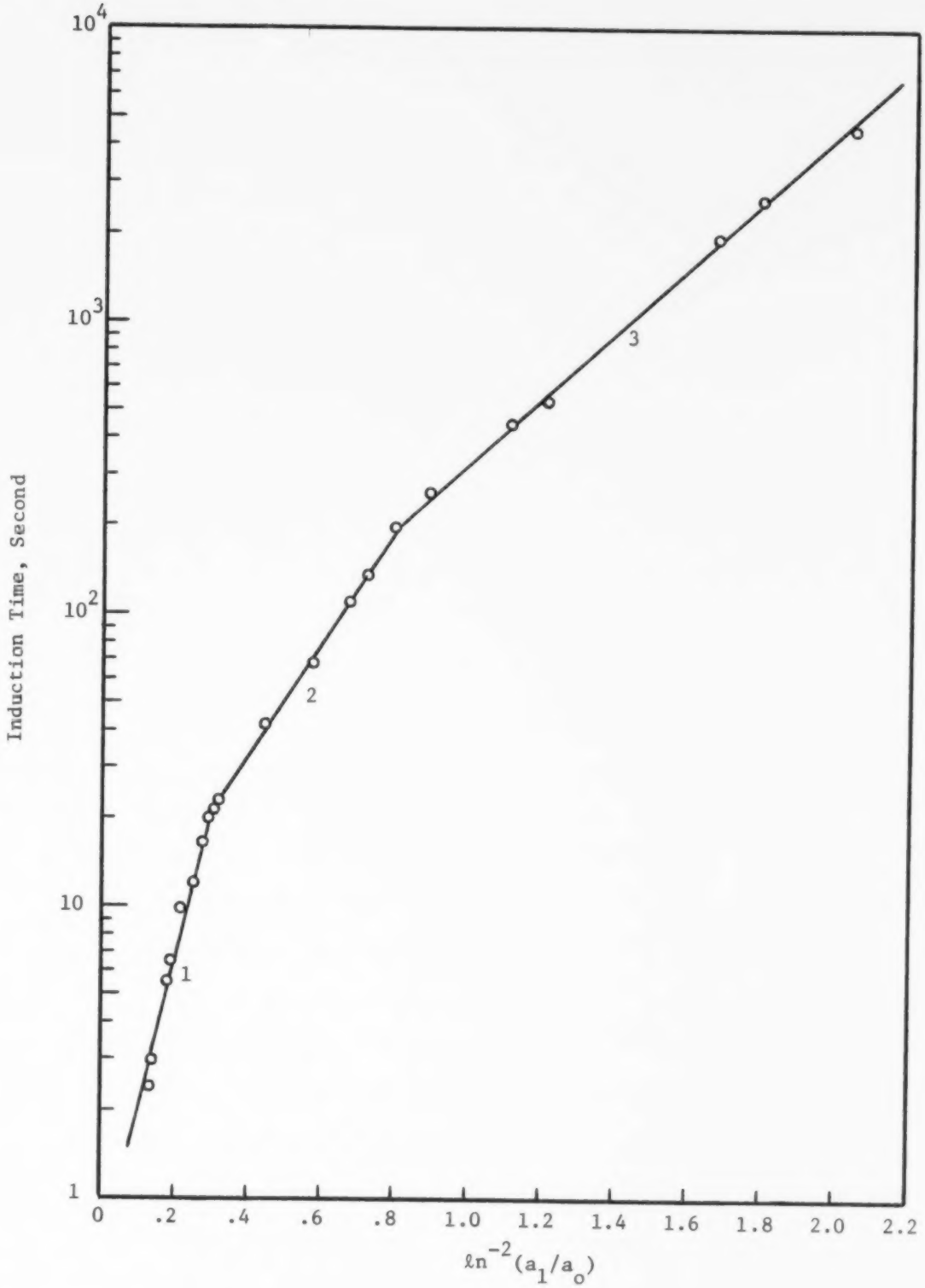

Figure 16. Induction Time of Aqueous Sodium Chloride Droplets on Spider Silk as a Function of $Ln^{-2}(a_1/a_o)$.

TABLE XVI. HETEROGENEOUS NUCLEATION FACTORS FOR AQUEOUS SODIUM CHLORIDE DROPLETS ON SPIDER SILK

	$\ell n^{-2}\left(\frac{a_1}{a_0}\right)$ range	B	C
Zone 1	0.1 - 0.3	$10^{0.21}$	12.0
Zone 2	0.3 - 0.8	$10^{-0.73}$	4.5
Zone 3	0.8 - 2.3	$10^{-1.40}$	2.6

another zone also existed for glass thread; this point was not shown in Figure 15 due to its large value for $\ell n^{-2}(a_1/a_0)$.

VIII. EFFECTS OF POLLUTANTS ON NUCLEATION

A. Effect of Lead Chloride on the Induction Time

Impurities have long been known to influence the normal growth pattern of crystals from alkali halides solutions.[62] Lead ions were found to be most active in the case of potassium chloride, and a small quantity of lead chloride significantly reduced the rate of crystal growth of potassium and sodium chloride.[63-69] The supersaturation at the crystallization point for potassium chloride was found to vary with the concentration of lead ions.[70] These data were obtained by cooling a potassium chloride solution in a beaker. The solution was stirred during the tests, and the crystallization points were detected by calorimeter. The effect of stirring is not known, so the data can only be used as an indication of the role of lead ions on nucleation by comparison to pure solution without lead ions. This technique is not suitable for sodium chloride solutions because the temperature coefficient of solubility of sodium chloride is very small. Induction periods cannot be obtained for a fixed solution concentration due to the constantly changing temperature.

Droplets of aqueous sodium chloride with lead chloride present were studied on spider silk. The results are presented in Table XVII. Induction periods were found to be two to three times longer in the presence of 100 ppm (moles $PbCl_2$/mole NaCl) at most supersaturation conditions. The effect of the lead ions further increases at lower supersaturations. The data with and without lead chloride are presented in Figure 17.

The effects of lead ions are not detectable in homogeneous nucleation, however. The data obtained are identical with and without the presence of lead chloride. The reason is unknown.

TABLE XVII. NUCLEATION DATA FOR AQUEOUS SODIUM CHLORIDE DROPLETS WITH AND WITHOUT LEAD CHLORIDE ON SPIDER SILK

Relative Humidity	Induction Period	
	Without $PbCl_2$	With 100 ppm $PbCl_2$
(%)	(sec)	(sec)
46.6	2	6
51.3	5	11
54.6	11	21
57.5	19	43
59.3	26	56
59.5	28	68
61.4	41	120
64.0	125	520
65.2	440	840
65.4	460	1100
66.5	650	6400
68.4	7200	100,000

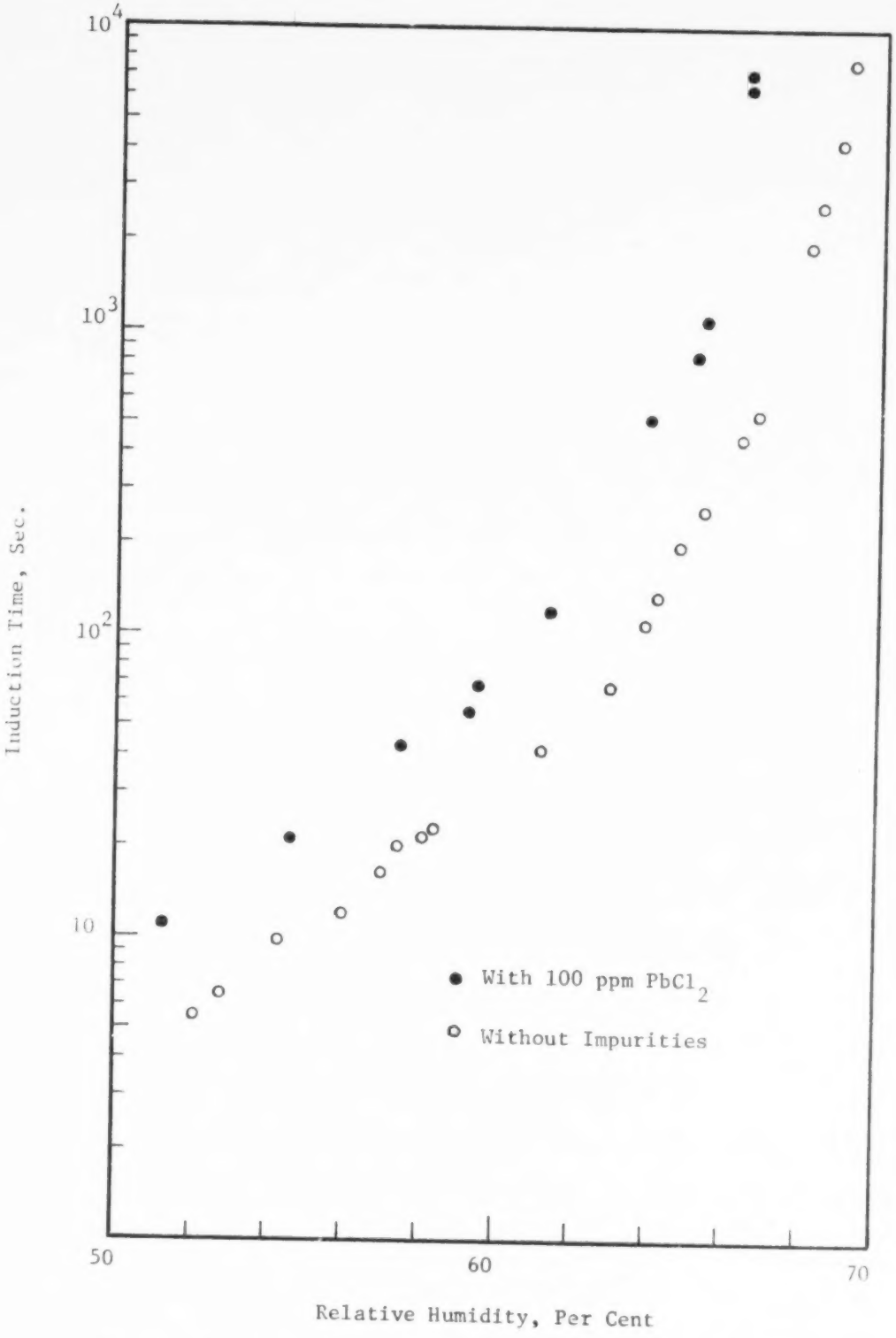

Figure 17. Effect of Lead Chloride on the Induction Time of Aqueous Sodium Chloride Droplets on Spider Silk.

B. Effects of Absorbed Gaseous Pollutants

Methylamine vapor and sulfur dioxide gas as additives were studied also. Methylamine altered the induction time in all tests. The main reason, apparently, is because it alters the dew point of the air in the system[71] thus changing the equilibrium state. The degree of supersaturation of the droplets could not be determined. Therefore, the specific effect of methylamine on the nucleation mechanism is not known. The effect of sulfur dioxide was not detectable. The effects must be very small even at concentration as high as 1,000 ppm. Droplets of aqueous sodium chloride were studied in the above experiments.

IX. DISCUSSIONS AND CONCLUSIONS

A. Experimental Methods

Two phenomena are of major concern in any study of homogeneous nucleation: the nucleation rate and the induction time. Nucleation rate at steady state has been much studied both theoretically and experimentally. Progress has been slow, however, because of complications involved in the determination of the number of critical clusters and the interfacial energy of the clusters. Critical comparison between theory and experiment for solution systems is rarely satisfactory.

Experimental studies of nucleation in the vapor phase are mostly accomplished by an expansion process. The vapor is cooled either by expansion in a piston cloud chamber[72,73] or upon passage through a supersonic nozzle.[74,75] Liquids and melts are studied by dispersion of fine droplets into another supporting liquid medium[76-86] or by mixing of reactants.[87-91] Nucleation study of bulk solution in a container[92-98] turns out to be heterogeneous nucleation, not homogeneous.

Quantitative testing of nucleation theory is not entirely feasible due to undesired factors in each of the methods noted above.[99-101] It is impossible to detect accurately the critical clusters as they are formed in a piston cloud chamber. Evaluation of the time required for the critical cluster to grow into a measurable size is not an easy task in itself. Transient heating of the gas from the walls and the fluid dynamics of the piston are two other problems.[21] Supersonic nozzle techniques share one of the problems of the cloud chamber method in that the growth of critical nuclei must be carefully considered. This method would be more reliable if the detecting technique were improved so that the number and size of nuclei could be measured for

smaller clusters than can now be done.

Heterogeneous nucleation is not avoided when droplets are dispersed in oil for study because the large sizes required for observation increase the likelihood of impurities in the droplets and there is the interface between the droplets and the supporting medium to alter the nature of the nucleation.[24] This method may give fair results when small droplets of melts or pure substances are studied provided the supporting medium does not interfere with the nucleation. The method is not suitable for solutions, especially aqueous sodium chloride solutions. Droplets as small as 2 microns in diameter[82] can be studied in one method which allows droplets to float in the underface at the cell cover. The rate of nucleation is determined from time-lapse photography employing a polarizing microscope. The surface of the cell may influence homogeneous nucleation. However, the effect is possibly small in the size range studied.

Rapid mixing of two solutions can establish a highly supersaturated solution before precipitating.[89,90] Here particle number concentration and induction time are measured as a function of supersaturation. Interfacial energies calculated from this type of experimental data seem to be of the right order of magnitude.[24,99,100] There are no other interfacial energy data for the same substances studied to compare with, however. Induction times measured by the mixing technique and used in the calculation of nucleation parameters were all less than 1 second.[88] The effects of the walls and the vortex action caused by the mixing may alter the nucleation process. Impurity particles may also play a part in the results.

Each of the methods has its own merits as well as its limitations and uncertainties. Homogeneous nucleation theory obviously cannot be verified

by any single technique known so far. Efforts up to the present have been concentrated on nucleation rate studies, both theoretical and experimental. Induction time has been studied very little and the errors caused by the walls and impurity particles are always questionable. Surface phenomena must be excluded before homogeneous nucleation of a solution can take place. All such catalytic effects tend to reduce the induction time and to yield low values for the interfacial energy and the kinetic constants. Another difficulty in any experimental study of a solution involves the achieving of of a supersaturated state rapidly without introducing catalytic effects. Cooling a solution in a container to a lower temperature involves cooling rate, surface effects, and non-uniformity temperature problems. The results reported vary from system to system and cannot be used to test the validity of any homogeneous nucleation theory.

The airborne droplet technique of this investigation seems to be satisfactory for induction time studies of solutions. Nucleation rates may also be studied providing the detecting system is satisfactory. When droplets are suspended in air, the only "surface" in contact with the solution is gaseous molecules. How much the gas-liquid interface influences homogeneous nucleation inside the droplets is not definitely known. If there is any effect, it should be much smaller than that of a liquid-liquid or a liquid-solid interface. The droplets are small so that the fraction of droplets containing impurity particles is small. This factor should barely affect the results because of the way the data are taken. Supersaturation conditions can be achieved rapidly, the time consumed being negligible when compared to the induction time. The most important point is that the variation in induction time is great. Kinetic constant and the interfacial emergy data can be

determined independently from the induction time data. Also, the time required for the critical nuclei to grow into complete crystals is so short at high supersaturations that the induction period may be taken as the time measured experimentally without correction.

In a bulk system, whether vapor or liquid, the degree of supersaturation of the mother phase changes when nucleation occurs. Also, secondary nucleation may interfere and confuse the homogeneous nucleation. These factors are not involved in the airborne droplet method employed in this study.

The merits of the airborne droplet technique may be summarized as follows:

1. Droplets are suspended in gas and the wall effect is avoided.
2. The supersaturation state of the droplets can be created rapidly and cooling rates need not be considered.
3. Supersaturation values for aqueous solutions can be determined from the equilibrium humidity at constant temperature and uniform conditions throughout the system can be maintained.
4. The droplet size studied is small so that the effect of impurities is negligible in the final measurements.
5. Operating procedures are simple. No counting is required.
6. Induction time measurements can cover wide intervals. Kinetic constant and the interfacial energy information can be determined from induction time.

There are also disadvantages of the method. Only certain substances can be studied and accurate physical property data for all components of the system must be available.

The apparatus used in this study can still be improved to yield higher

quality data. Nucleation rates could be better measured if a more sophisticated light scattering system were employed. The size of droplets must be small to eliminate settling effect.[5] The number concentration of the droplets has to be low to avoid coagulation. Nevertheless, the airborne droplet technique has the potential to be one of the most effective methods for studying homogeneous nucleation.

B. Properties of Electrolyte Solutions

Basic nucleation theory considers that molecular clusters form and grow by incorporating other molecules or monomers. The situation in aqueous solutions of electrolytes is quite different. The exact behavior of the ions, both cations and anions, and their relation with water molecules in supersaturated solutions are not well understood. It is evident that a cation, for example, will collide with and incorporate only an anion, a neutral molecule, or a neutral cluster. A cluster may grow by incorporating more ions or it may shrink by losing ions. In view of these processes, a factor may exist modifying the kinetic constants derived for systems containing only molecules or monomers. The exact magnitude of this factor cannot be evaluated until the behavior of supersaturated ionic solutions is well understood.

A simplified view is suggested here. A cluster containing even numbers of ions may collide with a non-ionized molecule or an ion. The sum of the numbers of molecules and ions existing in a solution is larger than the number of molecules if no disassociation occurs. Therefore, the probability of having a collision increases according to the degree of disassociation. If the entity colliding with a cluster is a molecule, then the cluster grows one molecule larger. But if the entity colliding with this cluster is an ion,

then the cluster must collide with another ion of the opposite sign to accomplish further growth. Two steps are involved in this case. The number of the ions having an opposite sign is equal to or less than the number of molecules in a solution with no disassociation of molecules.

The disassociation of solute molecules in the solvent may present problems for attempts to compare the measured kinetic constant with any existing nucleation theoretical models. Even if the factor has a magnitude of 0.1 or 10, it does not seem to be important at this time since it is not known whether the kinetic constant should be 10^{33} or 10^{50}.

The interfacial energies obtained represent values for the critical cluster at the interface between the cluster and the supersaturated solution. The disassociation mechanism should little affect the interfacial energy data since the latter were determined from data trends (slopes) and not from kinetic constants.

C. Effects of Impurities

Lead chloride was found to alter the induction time of droplets on surfaces but not of airborne droplets. It seems, therefore, that lead chloride interferes with the mechanism of heterogeneous nucleation but not of homogeneous nucleation. If this is always true, lead ions may be used to check whether or not a system is measuring true homogeneous nucleation. For example, nucleation studies of solution in a beaker or a test tube have long been suspected of being related to heterogeneous and not to homogeneous nucleation. This could be tested by including lead chloride in the system. Experimental results indicated that the nucleation temperatures of potassium chloride solutions in beakers varies with lead ion concentration.[70]

D. Induction Time

Homogeneous nucleation is a probability phenomenon. Nucleation may occur as soon as supersaturation is established. The fraction of droplets having undergone nucleation in time t may be expressed by

$$F = 1 - \exp[-AVP^{*}t] \tag{35}$$

where terms are defined in Section III. Theoretically, the probability of nucleation in a single droplet is greater as time increases. The induction time of a single airborne droplet may also vary substantially. Therefore, either a great number of droplets must be studied or many measurements made with a single droplet to establish the homogeneous nucleation process.

When droplets on surfaces were studied, all of them supported on a clean spider silk nucleated at nearly the same time. The size of the droplets did not seem to influence the induction time. In other words, the probability nature of homogeneous nucleation disappeared. The nucleation of eight sodium chloride droplets from 10 to 40 μm in diameter supported by a spider silk was observed under a microscope. This experiment was repeatedly made and the induction time of all eight droplets was identical. This simple experiment shows that the mechanism of heterogeneous nucleation is quite different from homogeneous nucleation.

Nucleation of small droplets is analogous to a footrace. Heterogeneous nucleation is a short distance sprint. Events start at the same time and all reach the finish line nearly together. Homogeneous nucleation is more like a long distance race where the runners reach the finish lines separated by a wide margin. The average speed of the runners corresponds to the kinetic constant while the distance of the race corresponds to the interfacial energy

of the critical cluster. Comparison between heterogeneous nucleation and homogeneous nucleation is thus very difficult. More studies are needed to further the knowledge of nucleation.

X. RECOMMENDATIONS

The airborne droplet technique has the potential for being a very effective method for studying homogeneous nucleation. The reliability of the measurements for hygroscopic materials may be improved by using more accurate humidity control and better measuring devices for precise particle size and number data. If the number of droplets having undergone nucleation can be determined as a function of time, equations derived in this study may be examined throughout the whole nucleation period instead of just the final stage. Nucleation rates may also be determined if the droplet size is properly controlled, preferably with the droplets being small and uniform. Solvents other than water should be investigated so that more substances can be studied. The activity of the solute must be accurately evaluated if nucleation theory is to be critically examined. It is believed that nucleation in molten salts and organic substances can also be studied by the airborne droplets technique with some apparatus modifications.

Homogeneous nucleation can also be studied from observation of the behavior of a single droplet suspended in gas. Many measurements would be required to obtain statistically reliable results. Nevertheless, the potential of the airborne droplet technique seems great. The primary question remaining is whether or not the interface between the gas and the droplet surface interferes with the true nature of homogeneous nucleation inside the droplet.

Heterogeneous nucleation might be studied for melts and solutions on surfaces of known properties by means of droplet techniques. The surface employed would have to be small. The possibility of having surface defects would thereby be greatly reduced.

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